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CONTROL TECHNIQUES FOR SULFUR OXIDE AIR POLLUTANTS

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U.S. DEPARTMENT OF HEALTH, EDUCATION, AND WELFARE
Public Health Service
Consumer Protection and Environmental Health Service

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FOR
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U.S. DEPARTMENT OF HEALTH, EDUCATION, AND WELFARE
Public Health Service
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National Air Pollution Control Administration
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Preface

Throughout the development of Federal air pollution legislation, the Congress has consistently found that the States and local governments have the primary responsibility for preventing and controlling air pollution at its source. Further, the Congress has consistently declared that it is the responsibility of the Federal government to provide technical and financial assistance to State and local governments so that they can undertake these responsibilities.

These principles were reiterated in the Air Quality Act of 1967. A key element of that Act directs the Secretary of Health, Education, and Welfare to collect and make available information on all aspects of air pollution and its control. Under the Act, the issuance of control techniques information is a vital step in a program designed to assist the States in taking responsible technological, social, and political action to protect the public from the adverse effects of air pollution.

Briefly, the Act calls for the Secretary of Health, Education, and Welfare to define the broad atmospheric areas of the Nation in which climate, meteorology, and topography, all of which influence the capacity of air to dilute and disperse pollution, are generally homogeneous.

Further, the Act requires the Secretary to define those geographical regions in the country where air pollution is a problem—whether interstate or intrastate. These air quality control regions are designated on the basis of meteorological, social, and political factors which suggest that a group of communities should be treated as a unit for setting limitations on concentrations of atmospheric pollutants. Concurrently, the Secretary is required to issue air quality criteria for those pollutants he believes may be harmful to health or welfare, and to publish related information on the techniques which can be employed to control the sources of those pollutants.

Once these steps have been taken for any region, and for any pollutant or combination of pollutants, then the State or States responsible for the designated region are on notice to develop ambient air quality standards applicable to the region for the pollutants involved, and to develop plans of action for meeting the standards.

The Department of Health, Education, and Welfare will review, evaluate, and approve these standards and plans and, once they are approved, the States will be expected to take action to control pollution sources in the manner outlined in their plans.

At the direction of the Secretary, the National Air Pollution Control Administration has established appropriate programs to carry out the several Federal responsibilities specified in the legislation.

Control Techniques for Sulfur Oxide Air Pollutants is one of the first of a series of documents to be produced under the program established to carry out the responsibility for developing and distributing control technology information. The document is the culmination of intensive and dedicated effort on the part of many persons.

In accordance with the Air Quality Act, a National Air Pollution Control Techniques Advisory Committee was established, having a membership broadly representative of industry, universities, and all levels of government. The committee, whose members are listed following this discussion, provided invaluable advice in identifying the best possible methods for controlling the sources of sulfur oxide air pollution, assisted in determining the costs involved, and gave major assistance in drafting this document.

As further required by the Air Quality Act, appropriate Federal departments and agencies, also listed on the following pages, were consulted prior to issuance of this document. A Federal consultation committee, comprising members designated by the heads of 17 departments and agencies, reviewed the document, and met with staff personnel of the National Air Pollution Control Administration to discuss its contents.

During 1967, at the initiation of the Secretary of Health, Education, and Welfare, several government-industry task groups were formed to explore mutual problems relating to air pollution control. One of these, a task group on control technology research and development, looked into ways that industry representatives could participate in the review of the control techniques reports. Accordingly, several industrial representatives, listed on the following pages, reviewed this document and provided helpful comments and suggestions. In addition, certain consultants to the National Air Pollution Control Administration also revised and assisted in preparing portions of this document. (These also are listed on the following pages.)

The Administration is pleased to acknowledge efforts of each of the persons specifically named, as well as those of the many not so listed who contributed to the publication of this volume. In the last analysis, however, the National Air Pollution Control Administration is responsible for its content.

The control of air pollutant emissions is a complex problem because of the variety of sources and source characteristics. Technical factors frequently make necessary the use of different control procedures for different types of sources. Many techniques are still in the development stage, and prudent control strategy may call for the use of interim methods until these techniques are perfected. Thus, we can expect that we will continue to improve, refine, and periodically revise the control techniques information so that it will continue to reflect the most up-to-date knowledge available.

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SUMMARY

SOURCES OF SULFUR OXIDES

Approximately three-fourths of the 28.6 million tons of sulfur oxides, largely sulfur dioxide (SO_2), emitted into the atmosphere of the United States in 1966 resulted from the combustion of sulfur-bearing fuels. Coal combustion accounted for the largest part of this total. Industrial processes, mainly smelting and petroleum refining, accounted for the remaining sulfur oxide emissions. The quantity of sulfur oxides emitted varies widely from area to area, depending on the type and quantity of fuel consumed and on the industrial processes.

Combustion Processes

The rapid growth of the economy of this country has been due, in part, to the ready supply of naturally occurring fossil fuels (coal, oil, and gas). These fuels currently supply about 95 percent of the 57 quadrillion (57×10^{15}) Btu consumed in the United States annually. Nuclear energy currently supplies only a small fraction of total energy, buts its contribution is expected to grow rapidly.

One of the best existing methods for reducing sulfur oxide emissions from fuel combustion sources is the use of low-sulfur fuels, such as natural gas, low-sulfur fuel oil, and low-sulfur coal; or by converting to another source of power such as hydropower or nuclear energy. Many economic and social factors would, however, be involved in any massive switch to low-sulfur fuels. Careful planning which takes into consideration the cost and availability of these fuels, as well as the levels and effects of emitted SO_2, can minimize these problems. Using low-sulfur fuels on a short-term basis during periods of severe air pollution may also be feasible.

Coal is by far our most abundant fossil fuel. Low-sulfur supplies of this fuel do exist, but they have not been fully developed nor are they very widely distributed. It is estimated that over 40 percent of the high-rank coals found east of the Mississippi River contain less than 1 percent sulfur (i.e., 95 billion tons). Approximately 50 percent of this 95 billion tons of coal should be recoverable. A premium price is usually paid for high-rank, low-sulfur coal. For areas not adjacent to low-sulfur coal supplies, additional transportation costs will constitute an increasing part of the delivered price.

Coal cleaning processes are capable of removing some of the pyrite sulfur in coal. Cleaning processes that include crushing to 1½ inches or less and flotation separation tend to remove more pyrite material. Because the degree to which a particular coal can be cleaned varies widely and depends on the amount and distribution of the pyrite sulfur in the coal, quantitative statements about coal cleanability, its cost, and the amount of cleanable coal available cannot be made.

Though under active research, none of the more elaborate coal processing schemes, such as gasification and liquefaction, are presently in full-scale operation. The current state of development of these processes is described in the Appendix.

Approximately 600 billion barrels of residual fuel oil (grades 5 and 6) are burned annually in the United States. More than 80 percent of this fuel contains at least 2 percent sulfur. The east-coast regions burn about 50 percent of this fuel oil, most of which is imported from South America. Due to the nature of petroleum refining processes, sulfur present in crude oil tends to be concentrated in the residual oil fraction.

Lighter fuel oils (grades 1 and 2) are currently being consumed at a rate of about 500 million barrels per year. The lighter oils generally contain between 0.04 and 0.6 percent sulfur, and burning them does not produce as much sulfur oxides as does burning residual oil. Because of the higher cost of this fuel it is not generally burned by large consumers such as utilities and large industrial plants.

Various refinery process schemes that can produce a residual fuel oil with sulfur content of 1.0 percent or less are currently being installed and some are in operation. These schemes use delayed coking, solvent de-asphalting, and hydrogen treating processes. Their principal product is low-sulfur distillate oil, which is blended with heavy oil fractions to produce a low-sulfur residual fuel oil. Desulfurizing to 1.0 percent costs about $.25 to $.75 per barrel ($.04 to $.12 per million Btu); however, the price of 1.0-percent-sulfur-content residual fuel oil is influenced by many factors, and prices to date have not in general increased greatly. Desulfurizing to less than 1.0 percent will become more feasible as these schemes are further improved.

Natural gas is now available in all parts of the country, and production has increased to about 18 trillion cubic feet per year. Sulfur compounds contained in natural gas are for the most part removed before marketing. This fuel, therefore, burns with negligible sulfur oxide emissions and is widely used. While new reserves of natural gas are being found, the domestic supply of this fuel at current prices will probably become limited before the turn of the century because of increased production costs.

Fuel costs vary widely and depend, among other things, on the consumer's location and demand. Fuel-cost data are presented in this report for industrial users in 50 Standard Metropolitan Statistical Areas for coal and oil of various sulfur contents, and natural gas. When calculating the various costs involved in fuel substitution schemes and the effect of the schemes on sulfur oxides emissions, the following steps must be taken:

1. Determine heating requirements in Btu per hour, of unit in question.
2. Select the various fuels that may be burned and determine their costs.
3. For the various fuels determine the cost of boiler modifications and operating expense.
4. Annualize the costs.
5. Determine the extent of sulfur dioxide emissions from combustion of the alternative fuels.

In areas where the cost of low-sulfur fuels is high and the supply limited, fuel substitution may not be an economically feasible method of reducing sulfur oxide emissions. This is especially true in the case of large fuel consumers, such as electrical generating stations. Increased attention has, therefore, been recently focused on methods for removing sulfur oxides from the flue gas before it enters the atmosphere. No flue gas desulfurization processes are presently in widespread use, but several methods such as alkalized alumina sorption, limestone-dolomite injection, and catalytic oxidation are currently under active investigation.

The limestone-dolomite injection process is the simplest method currently being developed for the control of SO_2 emissions from large combustion sources. In this process, limestone injected into the furnace reacts with the sulfur oxides to form calcium sulfate, a solid, which is removed by dust-collecting equipment. The degree of reaction can be increased by placing a scrubber on the system, since the limestone, which calcines to quicklime in the furnace, reacts fully in the scrubber due to increased contact and retention time. Sulfur oxide removal efficiencies in excess of 80 percent are obtainable when the scrubbing system is used. The primary disadvantage of this system is the large amount of waste material (calcium sulfate and sulfite, unreacted limestone, and fly ash) which must be disposed of. Flue gas reheating may be required when the scrubber is used.

Estimated costs for an 800-megawatt, coal fired power plant, operating at a load factor of 90 per cent are tabulated below.

Process	Capital cost	Operating cost, cents/kw-hr	Percent SO_2 removal
Limestone injection	$3,300,000	0.029	40–60
Limestone injection followed by wet scrubbing	$4,650,000	0.035	80–90

Three full-scale installations of the limestone-dolomite wet-scrubbing process are presently under way on coal-burning power plants in the 125- to 420-megawatt range, and one of these is now in the preliminary steps of operation. Two TVA power plants are also currently being modified for the dry limestone injection process.

The alkalized alumina process uses a dry sodium-aluminate metal oxide to contact and react with the sulfur dioxide in a special reactor. The reacted sorbent is then regenerated with a reducing gas and the sulfur reclaimed. This process, though more complicated than the limestone injection process, does produce a saleable byproduct in the form of sulfur. Sulfur dioxide removal efficiencies in excess of 90 percent have been obtained on pilot-scale plants.

Because of the large amount of equipment that must be installed for this process, it appears to be more adaptable to new installations. The cost of this system, although speculative at present, is estimated at $8.6 million capital investment for an 800-megawatt plant. Operating costs vary with the market for recovered sulfur.

Development of full-scale alkalized alumina process installations is dependent on additional pilot-scale work.

The catalytic oxidation process converts sulfur oxides in the flue gas to weak (75 to 80 percent) sulfuric acid by passing the gas stream through a vanadium pentoxide catalyst and a series of condensers. This process has advanced through the pilot-plant stage and is available from the developer.

For a new 800-megawatt plant the catalytic oxidation system would require an investment of between $16 million and $24 million. Operating costs would depend largely on the price obtained for sulfuric acid in that particular area. Transportation of this weak acid over long distances would not be economical.

Other flue-gas desulfurization processes are also being actively studied both here and abroad. These include the Beckwell scrubbing system, char sorption, and scrubbing with molten metallic salts.

The following table summarizes SO_2 control techniques for combustion processes.

SUMMARY OF METHODS FOR CONTROLLING SULFUR OXIDE EMISSIONS FROM STATIONARY COMBUSTION SOURCES

Method	*Remarks*
1. Change fuel or energy source.	1.
a. Switch to a fuel with lower sulfur content.	a. Fuel switching is being applied to all sizes of combustion units. Availability, applicability, and cost of the fuels with lower sulfur content are critical factors in applying this method. Sulfur oxide emission reduction is directly proportional to reduction of sulfur in fuel.
b. Switch to another energy source such as hydro-electric or nuclear energy.	b. Used currently by large electric generating stations only. Causes no sulfur oxide emissions.
2. Desulfurize fuel.	2.
a. Coal.	a. Coal cleaning techniques, which include crushing and flotation, are already being used to a limited extent. Sulfur reduction depends on the pyrite content of the coal. Approximately 30 percent of the sulfur can generally be removed. Cleanability and costs vary widely depending on the type of coal. More elaborate chemical processing of coal will yield low-sulfur fuels, but economically feasible techniques are still in the development stage.
b. Residual fuel oil	b. Catalytic treating with hydrogen removes sulfur from oil. Blending of low-sulfur-content distillate oils with residual oil also yields a fuel with a sulfur content of 1.0 percent or less. For a typical east coast imported residual fuel oil, a 60-percent sulfur reduction can be readily achieved and greater reductions are possible. Costs vary widely, but are on the order of \$0.25 to \$0.75 per barrel (\$0.04-\$0.12 per million Btu).
3. Remove sulfur oxides from flue gas	3.
a. Limestone-dolomite injection, dry process	a. Calcined limestone reacts with sulfur oxides and is removed by fly ash control equipment, A large-scale prototype unit will be in operation in 1969. SO_2

Method	*Remarks*
	removal efficiencies between 40 and 60 percent are expected with operating costs on the order of 0.029 cents per kw-hr ($0.03/$10^6$ Btu).
b. Limestone-dolomite injection, wet process	b. Sulfur oxides react with the calcined limestone before entering a wet scrubber where further removal is achieved. This process is presently being installed on a number of power plants in the 125 to 420 Mw size range. SO_2 removal efficiencies between 80 and 90 percent may be obtained with an operating cost of about 0.035 cents per kw-hr ($0.036/$10^6$ Btu) for an existing plant.
. Alkalized alumina sorption	c. Presently only in the pilot-plant stage, this process removes sulfur oxides by sorption on the solid metal oxide. The metal oxide is then regenerated and sulfur is recovered. Removal of at least 90 percent of the sulfur oxides is expected. Operating costs may be partially recovered when the sulfur is sold.
d. Catalytic oxidation	d. Sulfur dioxide is catalytically oxidized to SO_3 and recovered as condensed sulfuric acid. Removal of about 90 percent of the sulfur oxides is possible. Net operating costs will depend on the scale of recovered sulfuric acid.
e. Caustic scrubbing	e. In operation on a few small combustion processes, costs and removal efficiencies vary widely depending on specific operating conditions.
4. Increase combustion efficiency	4. Increased combustion efficiencies will reduce the amount of fuel burned and, thereby, decrease sulfur oxide emissions.

Industrial Processes

Nonferrous primary smelting of sulfide-containing metallic ores such as copper, zinc, and lead is the largest industrial-process emitter of sulfur dioxide, and currently accounts for emissions of about 3.5 million tons per year. Large modern smelters reduce these emissions by passing the exit gases through a sulfuric acid plant; they recover a valuable by-product in the form of sulfuric acid. The sulfuric acid plants are of the contact type and are adaptable to most smelter gases after the entrained solid matter has been removed. Installation of a sulfuric acid plant will usually reduce emissions by more than 90 percent. At times, smelter operating costs may be offset by marketing the recovered sulfuric acid. About half the primary smelters in this country presently use sulfuric acid recovery. These smelters use 42 percent of all the ore concentrate produced in the country.

Petroleum refineries, because of their increasing capacities and consumption of fuel, have become major sources of sulfur oxide emissions. Large quantities of low-grade, sulfur-bearing gas and liquid fuels generated in the refining processes, are used as fuel at the refinery. Removal of sulfur compounds from these fuels and from the petroleum feedstock by hydrogen treating and subsequent recovery of raw sulfur is possible and is practiced at many large refineries.

Recovery of hydrogen sulfide (H_2S) generated in the sulfur removal processes is readily accomplished by scrubbing the H_2S stream with ethanolamine or a similar solution. In this process, the H_2S is stripped from the recovery solution by heating. The rich H_2S gas is then converted to sulfur in a conventional Claus-type process. The cost of sulfur produced in a two-stage Claus-type recovery plant varies with plant size, but is much less than the cost of sulfur produced by conventional methods.

Sulfuric acid plants, by the very nature of the process, are emitters of SO_2 and sulfuric acid mist. These emissions can be decreased through improved plant design and operation. By increasing SO_2 to SO_3 conversion efficiencies from 96 to 98 percent, emissions are reduced from about 50 to about 25 pounds of SO_2 per ton of acid produced.

The double contact sulfuric acid manufacturing process incorporates an intermediate absorption tower before a final fourth catalytic conversion stage. This process can reduce emissions to about 5 pounds of SO_2 per ton of acid and increases plant yield. A number of these plants have been built in Europe.

The manufacture of coke, steel, and wood pulp, in addition to some other miscellaneous sources of sulfur oxides are not major sources nationally, but may be large local sources. Sulfur dioxide is not usually controlled at these sources; however, existing control methods such as scrubbers can be applied. Sulfur oxide emissions resulting from various waste disposal processes are not usually a problem except for those associated with burning coal waste.

Dispersion

Dispersion of sulfur oxides by tall stacks can be a useful approach toward reducing the frequency of high concentrations at ground level in some areas. The usefulness of the approach is limited by local meteorological and topographic conditions and by other sources of sulfur oxides in the area. Data presented on the cost of tall stacks show expenditures in excess of $2 million would be required for most large stacks over 900 feet tall. An extensive bibliography on gas dispersion is included in this report.

1. INTRODUCTION

Pursuant to authority delegated to the Commissioner of the National Air Pollution Control Administration, *Control Techniques for Sulfur Oxide Air Pollutants* is issued in accordance with Section 107c of the Clean Air Act (42 U.S.C. 1857c-2b1).

Sulfur oxides in the atmosphere are known to have many adverse effects upon health and welfare, and reduction of emissions of this class of pollutants is of prime importance to any effective air pollution abatement program. Sulfur oxide pollutants originate from a variety of sources, and the emissions vary widely in physical and chemical characteristics. Similarly, the available control techniques vary in type, application, effectiveness, and cost.

The control techniques described herein represent a broad spectrum of information from many engineering and other technical fields. Many of the devices, methods, and principles have been developed and used over many years, and much experience has been gained in their application. They are recommended as the techniques generally applicable to the broad range of sulfur oxides emission control problems. A discussion of other methods, still in various stages of research and development, serves to provide information about the latest concepts under consideration, even though they may not, as yet, be available for general use.

The proper choice of a method, or combination of methods, to be applied to any specific source depends on many factors other than the characteristics of the source itself. While a certain percentage of control, for example, may be acceptable for a single source, a much higher degree may be required for the same source when its emissions blend with those of others. This document provides a comprehensive review of the approaches commonly recommended for controlling the sources of sulfur oxides air pollution. It does not review all possible combinations of control techniques that might bring about more stringent control of each individual source.

The many commercial, domestic, industrial, and municipal processes and activities that generate sulfur oxide air pollutants are described individually in this document. The various techniques that can be applied to control emissions of sulfur oxides from these sources are reviewed and compared. Consideration of the availability and potential use of different fuels forms a major segment because, at the present time, means have not yet been perfected for effectively removing sulfur oxides from the flue gases of fuel-burning installations. Sections on source evaluation, equipment costs and cost-effectiveness analysis, and current research and development also are included. The bibliography comprises important reference articles, arranged according to applicable processes.

While some data are presented on quantities of sulfur oxides emitted to the atmosphere, the subject of the effects of sulfur oxides on health and welfare are considered in a companion document, *Air Quality Criteria for Sulfur Oxides.*

2. DEFINITIONS AND MEASUREMENTS OF SULFUR OXIDES

An oxide of sulfur is any chemical combination of sulfur and oxygen. This report, however, deals with only two such oxides, sulfur dioxide (SO_2) and sulfur trioxide (SO_3), which are the most common sulfur oxide pollutants. Sulfur dioxide is an invisible, nonflammable, acidic gas. It oxidizes to SO_3 in the atmosphere at varying rates, depending on temperature and the presence of other substances. Sulfur trioxide is a highly hygroscopic gas, which combines with water in the atmosphere to form sulfuric acid mist (H_2SO_4), or with other materials in the atmosphere to form sulfate compounds.

Atmospheric concentrations of SO_2 may be determined by manual or automatic methods.[1,2] A commonly used manual method is the p-rosaniline or West-Gaeke technique. Continuous monitoring instruments that sample, analyze, and continually record atmospheric SO_2 concentrations are commercially available. Sulfation of exposed lead peroxide paste and the sulfate content of atmospheric particulates are other indications of the presence of sulfur oxides in the air.

REFERENCES FOR SECTION 2

1. "Methods of Measuring and Monitoring Atmospheric Sulfur Dioxide." U.S. Dept. of Health, Education, and Welfare, National Center for Air Pollution Control, PHS-Pub-999-AP-6, Aug. 1964.
2. American Society for Testing Materials, Method D 1355-60.

3. MAJOR SOURCES OF SULFUR OXIDES

Sulfur oxides, primarily SO_2, are generated during the combustion of any sulfur-bearing fuel, and by many industrial processes that use sulfur-bearing raw materials. In 1966, about 28.6 million tons of SO_2 was emitted in the United States. The various sources of SO_2 are shown in Figure 3-1.

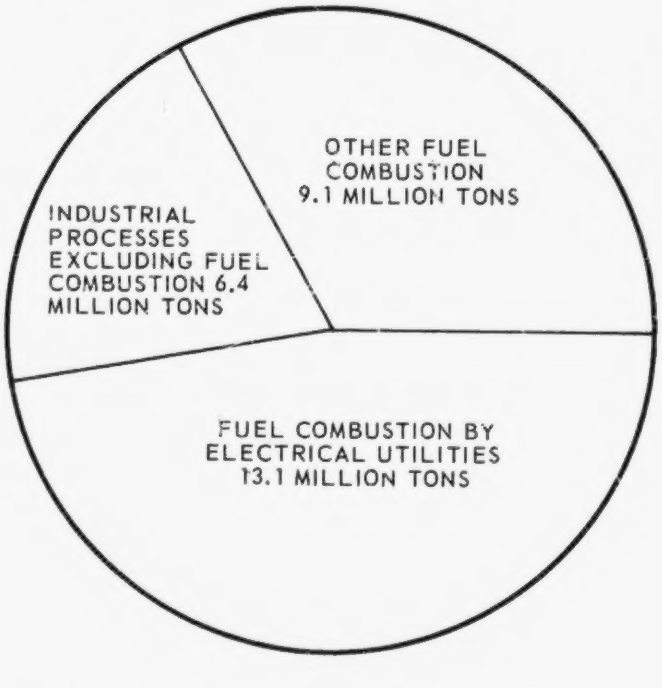

Figure 3-1. Nationwide sources of sulfur dioxide emissions, 1966.[1,2]

The distribution of emissions by source category in any particular city or specific location may differ markedly from that shown.

Figure 3-2 shows the estimated increase in SO_2 emissions with the passage of time if no air pollution controls were to be applied. This increase is largely due to the projected increase in fuel consumption by utility companies, which, it is expected, will level off in 1990, as nuclear power stations replace more fuel burning plants.

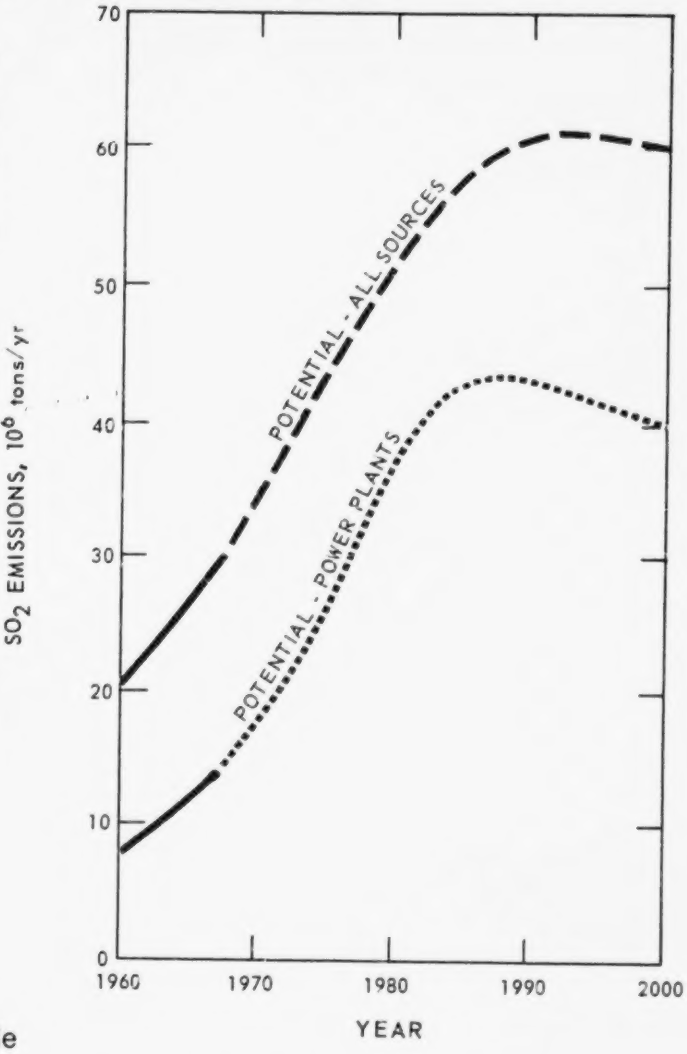

Figure 3-2. Estimated SO_2 emissions.[3]

3.1 COMBUSTION SOURCES

Combustion of fuels accounts for 77 percent of all SO_2 emitted. This is due to the relatively high sulfur content of some bituminous coals and residual fuel oils, and to the very large amounts of these fuels consumed in this country. Bituminous coal and residual fuel oil usually contain from 1 to 3 percent sulfur by weight. Combustion of these fuels produces about 2 pounds of SO_2 and about 0.03 pound of SO_3 for each pound of sulfur in the fuel.

Table 3-1. SO_2 EMISSIONS FROM FUEL COMBUSTION IN 1966[2]

Sources	SO_2 emissions, tons
Utility coal	11,925,000
Utility oil	1,218,000
Other coal	4,700,000
Other oil	4,386,000
Natural gas[a]	3,500
Total	22,232,500

[a] Not included in Reference 2.

Data on SO_2 emissions from fuel combustion in 1966 are presented in Table 3-1.

3.2 INDUSTRIAL PROCESS SOURCES

Smelting of metallic ores and oil refinery operations are the major industrial process sources of SO_2 emissions. Increased demand for sulfur and sulfuric acid should result in a more profitable recovery market for these emissions, tending to prevent any large, future increase of SO_2 emissions from these sources.

Sulfur dioxide emissions from industrial process sources in 1966 are given in Table 3-2.

Table 3-2. SO_2 EMISSIONS FROM INDUSTRIAL PROCESS SOURCES IN 1966[3]

Sources	SO_2 emissions, tons
Ore smelting	3,500,000
Petroleum	1,583,000
Sulfuric acid manufacturing	550,000
Coke processing	500,000
Refuse burning	200,000
Miscellaneous[a]	75,000
Total industrial process	6,408,000

[a] Includes chemical manufacturing, and pulp and paper production.

REFERENCES FOR SECTION 3

1. Hangebrauck, R. P. and Spaite, P. W. "A Status Report on Controlling the Oxides of Sulfur." J. Air Pollution Control Assoc., Vol. 18, pp. 5–8, Jan. 1968.
2. Rohrman, F. A. and Ludwig, J. H. Unpublished data, U.S. Dept. of Health, Education, and Welfare, National Center for Air Pollution Control.
3. Rohrman, F. A. and Ludwig, J. H. "SO_2 Pollution: The Next 30 Years." Power, pp. 82–83, May 1967.

4. CONTROL TECHNIQUES FOR FUEL COMBUSTION PROCESSES

4.1 ENERGY SOURCES, CONSUMPTION, AND USAGE TRENDS

The selection of an energy source depends upon the projected use, the competitive ability of producers of the raw energy (including electricity) to deliver the energy to the consumer, availability of the various raw energy forms, and preference of the consumer. Another factor is the effect on ambient air quality. Substitution of a low-air-pollution-potential energy source for a high-potential one is an effective method of reducing emissions of various air contaminants, including sulfur oxides.

As shown in the previous chapter, the combustion of coal and petroleum products (not including natural gas) accounted for approximately 22,229,000 tons, or 77 percent, of the emissions of SO_2 in the United States in 1966. Combustion of fuel for utility power generation is the largest source category, accounting for 45.5 percent of the total emissions of SO_2. In the Washington, D.C., metropolitan area, for example, the combustion of fuel for utility power generation accounted for 63 percent of the area's total SO_2 emissions.[1] In other areas, such as the Pacific Northwest, fuel combustion may account for little or no sulfur oxide emissions. If projected fuel use trends prove valid, and no changes in the sulfur content of fuels or in SO_2 control practices occur, then SO_2 emissions will more than double by the year 2000.

The United States consumes more energy than any other single nation. The annual energy consumption has increased from 101.3 million Btu per capita in 1850[2] to 278 million Btu per capita in 1965.[3] The corresponding total energy consumption has increased from $2{,}357 \times 10^{12}$ Btu per year in 1850[2] to $53{,}785 \times 10^{12}$ Btu per year in 1965.[3]

Table 4–1 shows the consumption of energy by major sources and consuming sectors from 1947 through 1966. The data indicate that the long-term consumption of coal has declined while consumption of petroleum, natural gas, hydropower, and nuclear power all have increased. Trends in electrical generation indicate that coal is the major fuel used and that its use has continued to increase in that category. Although electrical generation by nuclear power was begun in 1956, it was 1960 before it accounted for 0.1 percent of the production.

Long-range forecasts of energy requirements and fuel-use patterns are approximations. The forecasts include a wide range of assumptions and judgments regarding population growth, per capita consumption, changes in technology of use, economic developments, and availability of the several fuels.

Before 1962, the projected total energy consumption for the year 1980 ranged from 60×10^{15} to 145×10^{15} Btu (an average of 82×10^{15} Btu). Estimates for the year 2000 range from 105×10^{15} to 280×10^{15} Btu.[5] More recent estimates for 1980 range from 82×10^{15} to slightly less than 100×10^{15} Btu.[6-10] The total annual energy consumption per capita is predicted to increase from 278×10^{6} Btu in 1965 to 415×10^{6} Btu in 1985.[9]

The data in Figure 4–1 show that consumption of most energy sources will continue to increase and that nuclear energy will have the greatest rate of increase. In 1964, Landsberg[11] predicted for the years 1980 and 2000 the energy requirements and fuel-use patterns for commercial, residential, and industrial markets in the United States. These predictions, which now seem somewhat conservative, are presented in Figures 4–2 through 4–4. The electric generating capacities, by energy source for the year 1966, projected for the years 1980 and 2000, are presented in Figure 4–5.[6, 12, 13]

Other, more recent estimates[13] predict that

Table 4-1. CONSUMPTION OF ENERGY RESOURCES BY MAJOR SOURCES AND CONSUMING SECTORS[3,4]

[10^{12} Btu]

	1966	1965	1964	1963	1962	1961	1959[a]	1957	1955	1953	1950	1947
Household and commercial:												
Anthracite	143	168	85	103.0	121.1	128.8	192.2	271.0	330.7	457.2	660.4	812.8
Bituminous and lignite	573	546	560	671.0	798.6	782.9	814.9	981.3	1,443.7	1,614.8	2,252.5	2,585.5
Natural gas	5,945	5,518	5,314	5,026.8	4,849.2	4,478.8	4,023.8	3,390.9	2,849.5	2,293.7	1,641.7	1,125.0
Petroleum[b]	5,769	5,634	5,170	5,257.8	5,227.1	5,028.1	4,718.6	4,068.6	4,001.0	3,391.2	3,038.1	2,250.9
Hydropower	0	0	0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Nuclear	0	0	0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Total	12,432	11,867	11,149	11,058.6	10,996.0	10,416.6	9,749.5	8,711.8	8,624.9	7,756.9	7,592.7	6,774.2
Industrial:												
Anthracite	88	101	46	56.7	49.0	46.2	54.9	66.3	52.7	48.3	127.0	284.7
Bituminous and lignite	5,806	5,640	5,362	5,014.6	4,761.6	4,693.7	4,691.8	5,792.4	5,976.1	6,056.9	5,830.4	7,013.6
Natural gas	8,105	7,671	7,397	6,775.9	6,293.2	6,024.7	5,689.8	5,118.1	4,675.1	4,303.5	3,546.5	2,874.7
Petroleum[b]	4,334	4,138	4,184	3,994.0	3,879.7	3,682.1	3,458.1	3,477.8	3,329.0	3,092.0	2,641.5	2,489.7
Hydropower	0	0	0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Nuclear	0	0	0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Total	18,333	17,550	16,989	15,841.2	14,983.5	14,446.7	13,894.6	14,454.6	13,853.0	13,500.7	12,145.4	12,662.7
Transportation:												
Anthracite	0	0	0	0.0	0.0	0.0	7.4	9.2	11.6	12.7	19.6	23.9
Bituminous and lignite	18	19	20	19.1	19.5	21.7	99.8	268.3	462.1	796.3	1,681.3	3,006.2
Natural gas	553	517	448	438.6	395.8	390.8	361.6	309.7	253.8	238.4	129.9	0.0
Petroleum[b]	12,785	12,179	11,791	11,506.1	11,000.9	10,575.2	9,923.1	9,649.0	9,109.3	8,157.8	6,785.0	5,760.5
Hydropower	0	0	0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Nuclear	0	0	0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Total	13,356	12,715	12,259	11,963.8	11,416.2	1[illegible],987.7	10,391.9	10,236.2	9,836.8	9,205.2	8,615.8	8,790.6
Electricity generation, utilities:												
Anthracite	56	55	57	54.7	58.2	63.7	67.0	85.4	81.5	91.4	91.7	89.5
Bituminous and lignite	6,341	5,825	5,353	5,016.9	4,580.0	4,311.1	3,989.4	3,796.1	3,402.1	2,714.1	2,135.9	1,994.4
Natural gas	2,692	2,392	2,403	2,217.9	2,034.4	1,889.2	1,684.0	1,384.9	1,193.6	1,070.4	650.9	386.1
Petroleum[b]	905	744	636	599.8	579.0	577.0	545.9	512.4	512.2	577.1	662.2	468.0
Hydropower	2,060	2,049	1,873	1,910.0	1,943.0	1,777.0	1,695.0	1,568.0	1,497.0	1,550.0	1,601.0	1,459.0
Nuclear	58	39	34	31.1	25.9	19.2	11.7	1.2	0.0	0.0	0.0	0.0
Total	12,112	11,104	10,356	9,830.4	9,220.5	8,637.2	7,993.0	7,348.0	6,686.4	6,003.0	5,141.7	4,397.0

Miscellaneous and unaccounted for:												
Anthracite	3	4	177	146.2	134.9	165.1	156.0	96.4	122.0	101.6	114.8	13.3
Bituminous and lignite	0	0	0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Natural gas	0	0	0	383.8	454.4	446.5	231.1	212.6	260.1	250.0	181.0	132.6
Petroleum [b]	599	545	585	592.3	580.3	624.6	1,101.3	862.2	572.3	879.9	362.2	397.9
Hydropower	0	0	0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Nuclear	0	0	0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Total	602	549	1,762	1,122.3	1,169.6	1,236.2	1,488.4	1,171.2	955.3	1,231.5	658.0	543.8
Total gross energy:												
Anthracite	290	328	365	360.6	363.2	403.8	477.5	528.3	599.4	711.2	1,013.5	1,224.2
Bituminous and lignite	12,740	12,030	11,295	10,721.6	10,159.7	9,809.4	9,595.9	10,838.1	11,104.0	11,182.1	11,900.1	14,599.7
Natural gas	17,295	16,098	15,562	14,843.0	14,027.0	13,228.0	11,990.3	10,416.2	9,232.0	8,156.0	6,150.0	4,518.4
Petroleum [b]	24,392	23,241	22,386	21,950.0	21,267.0	20,487.0	19,747.0	18,570.0	17,524.0	16,098.0	13,489.0	11,367.0
Hydropower	2,060	2,049	1,873	1,910.0	1,943.0	1,777.0	1,695.0	1,568.0	1,497.0	1,550.0	1,601.0	1,459.0
Nuclear	58	39	34	31.1	25.9	19.2	11.7	1.2	0.0	0.0	0.0	0.0
Total	56,835	53,785	51,515	49,816.3	47,785.8	45,724.4	43,517.4	41,921.8	39,956.4	37,697.3	34,153.6	33,168.3

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[a] Total gross energy includes Alaska and Hawaii beginning in 1959.

[b] Natural gas liquids included with petroleum.

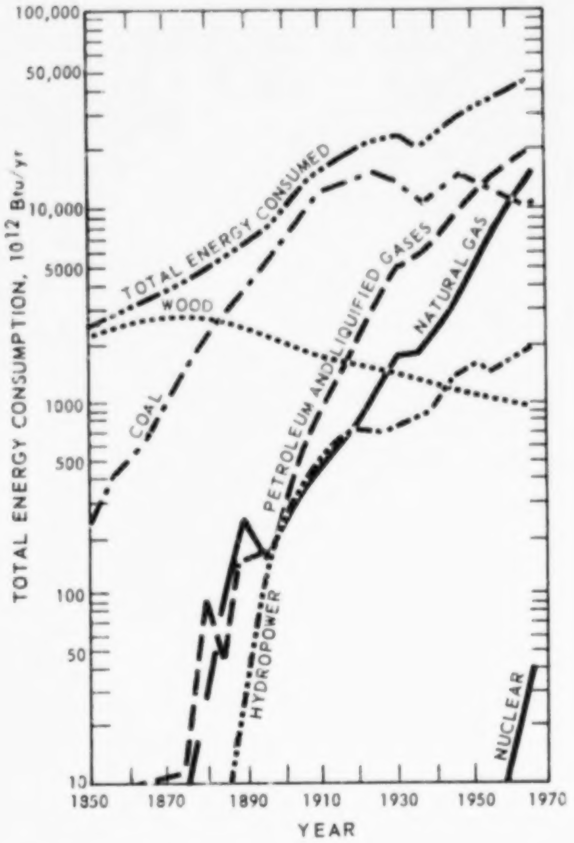

Figure 4-1. Trends in energy consumption by source, 1850 - 1965.[2,3]

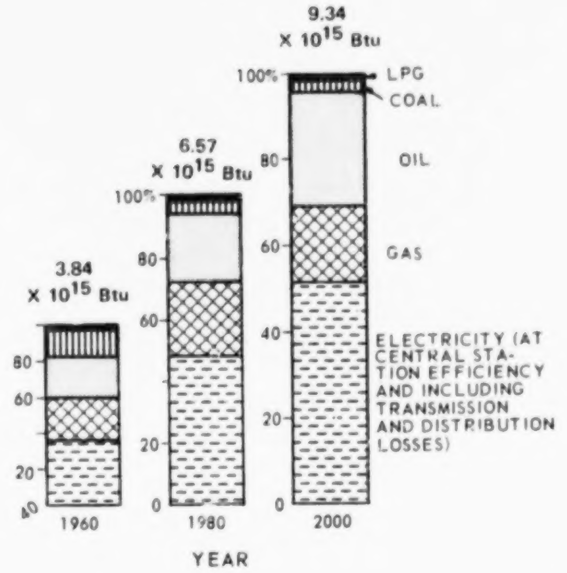

Figure 4-2. Future energy requirements and fuel-use patterns for the commercial market.[11]

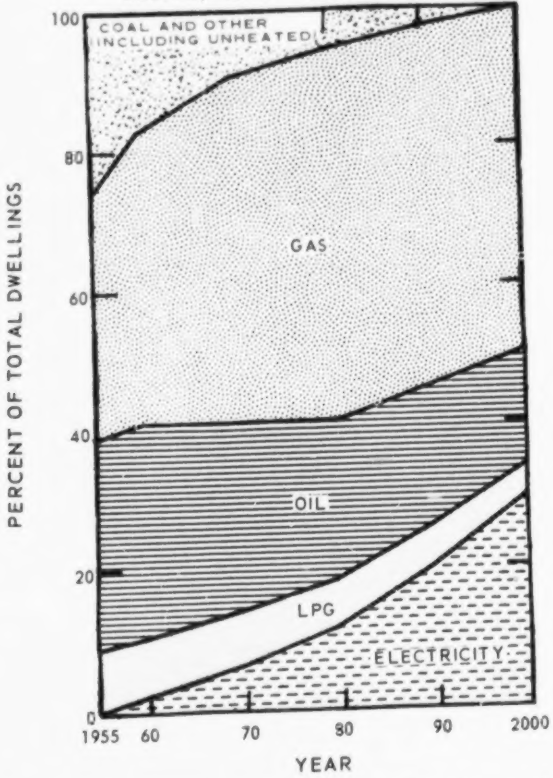

Figure 4-3. Future fuel-use patterns for residential home heating.[11]

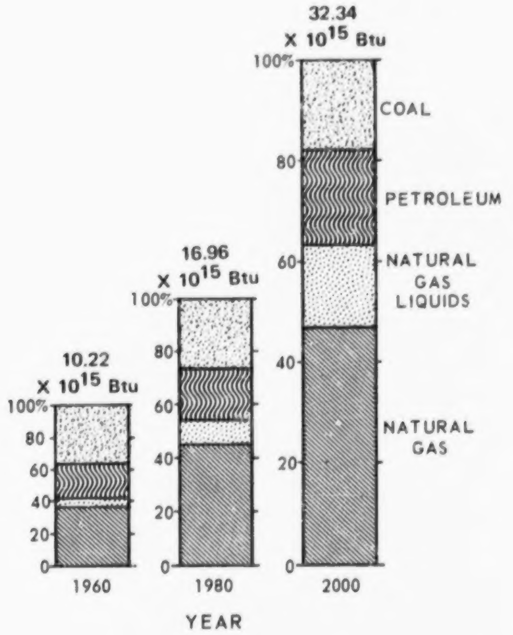

Figure 4-4. Future energy requirements and fuel use patterns for industrial use (except electricity).[11]

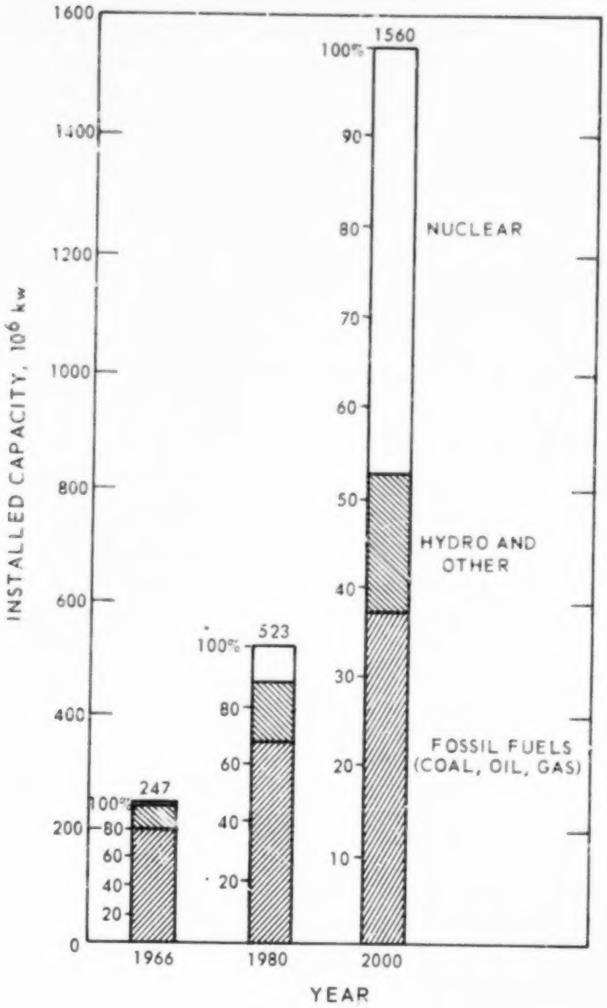

Figure 4-5. Trends in electrical power generation.[6, 12, 13]

the 1980 nuclear capacity of electrical utilities will be approximately 150,000 megawatts, or 25 percent of the total electrical capacity. It is estimated that by the year 2000, the nuclear capacity will account for more than half of the Nation's electrical generating capacity.

4.2 ENERGY AVAILABILITY

4.2.1 Coal

In the United States, estimated recoverable reserves of coal comprise approximately 83 percent of all fossil fuels in terms of energy equivalents.[14] Figure 4–6 is a map showing the coal producing areas in the United States. Figure 4–7 shows the estimated original and remaining coal reserves by rank as of January 1, 1965.

The use of the term "coal reserve" has very little meaning unless it is further described. "Estimated original coal reserve" is defined as the initial coal reserve before any was ever produced. "Remaining coal reserve" means the amount that is underground as of the date of the estimate. "Recoverable coal reserve" is the amount of coal underground, as of the date of the estimate, that can probably be mined in the future. These estimates include only that coal which is in seams that are 14 inches thick or more and occurs at depths of 3,000 feet or less. All of this recoverable coal may, however, not be economically mineable. Bituminous coal is currently being recovered from active mines at an efficiency of approximately 57 percent.[15]

Sulfur content of remaining coal reserves is an important factor in air pollution control. Table 4–2 shows the remaining reserves of coal of all ranks as of January 1, 1965, by range of sulfur content and by State. These estimates indicate that approximately two-thirds of the estimated reserves consist of low-sulfur (1.0 percent or less) coal; however, more than half is composed of low-rank coals (subbituminous and lignite). Considering only high-rank coals (bituminous and anthracite), the States east of the Mississippi River contain slightly over 40 percent (95×10^9 tons) of the coals containing 1.0 percent sulfur or less. These data are based largely on the analysis of cleaned coals.

In dealing with fuel sulfur content, it is important to note that an average sulfur content may be quite misleading in that it does not give any information on the range of sulfur values actually encountered. A range of sulfur contents or a maximum value should, therefore, be considered in specifying sulfur limits for fuels.

Approximately 98 percent of the total lignite reserves, which are largely low in sulfur, are located in North Dakota and Montana. Reserves of low-sulfur subbituminous coals are also located in the Western States, with about 60 percent of the total occurring in Montana and Wyoming.

Extra-high-voltage transmission of electricity and developments in the technology of using low-rank coal as a practical and economical fuel make it possible to have large

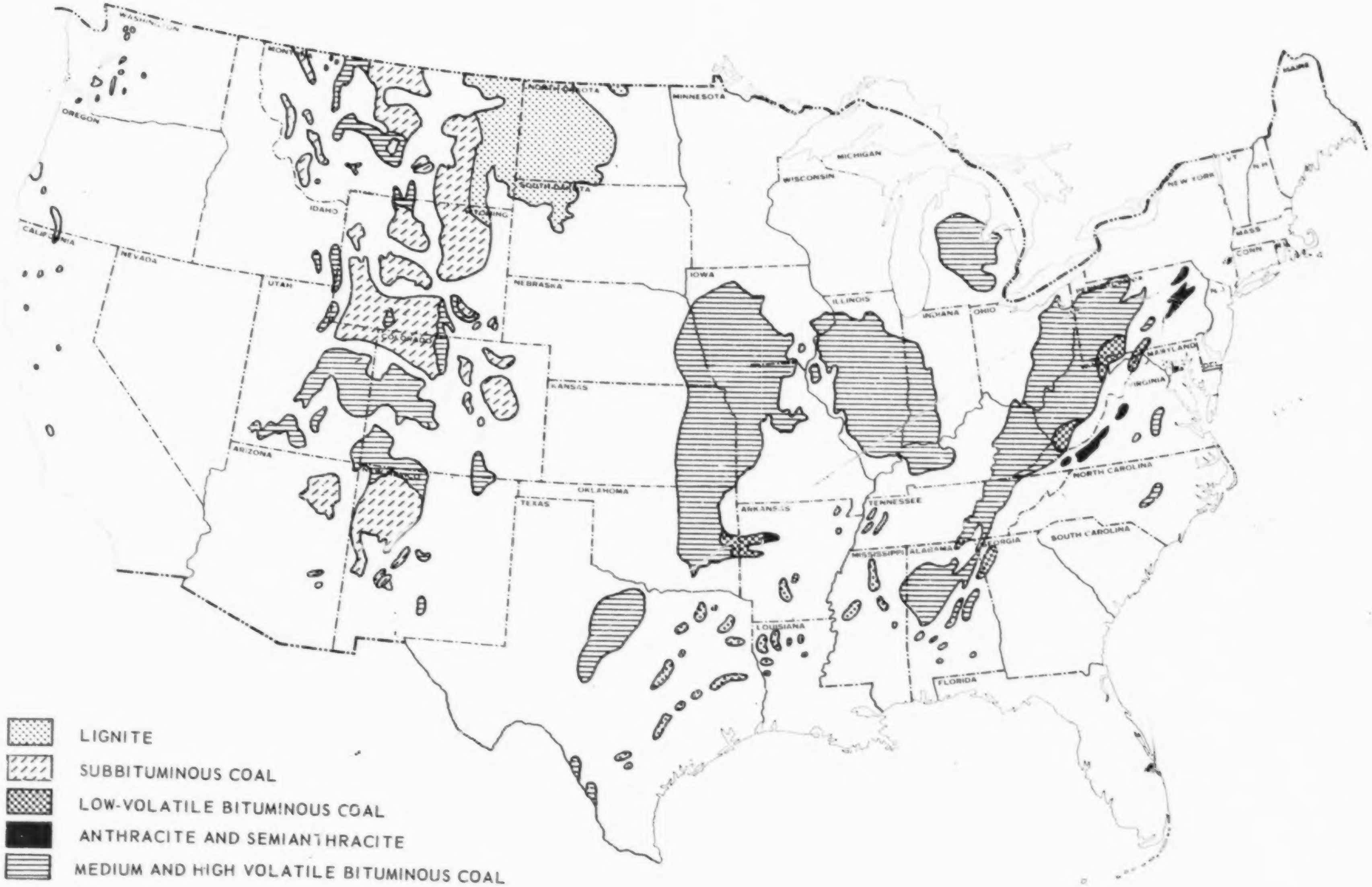
LIGNITE
SUBBITUMINOUS COAL
LOW-VOLATILE BITUMINOUS COAL
ANTHRACITE AND SEMIANTHRACITE
MEDIUM AND HIGH VOLATILE BITUMINOUS COAL
WASHINGTON
OREGON
CALIFORNIA
NEVADA
IDAHO
MONTANA
UTAH
ARIZONA
COLORADO
WYOMING
NORTH DAKOTA
SOUTH DAKOTA
NEBRASKA
KANSAS
OKLAHOMA
TEXAS
MINNESOTA
IOWA
WISCONSIN
MICHIGAN
ILLINOIS
INDIANA
OHIO
ARKANSAS
LOUISIANA
TENNESSEE
MISSISSIPPI
ALABAMA
GEORGIA
FLORIDA
SOUTH CAROLINA
NORTH CAROLINA
VIRGINIA
MARYLAND
NEW YORK
VT
N.H.
MAINE
MASS
CONN

Figure 4-6. Coal fields of the United States.[16]

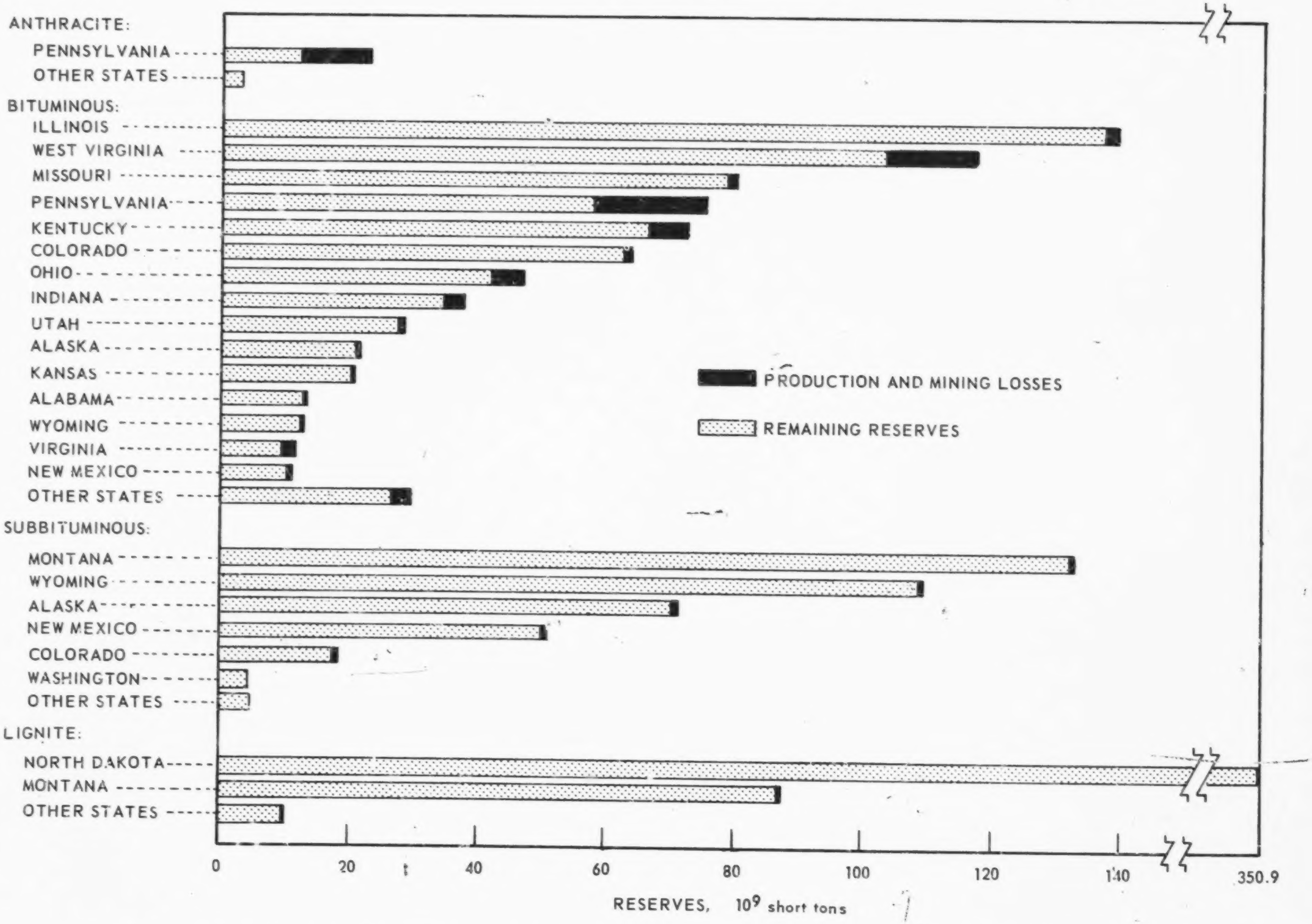

Figure 4-7. Estimated original and remaining coal reserves, by rank, in United States, January 1, 1965.[14]

Table 4-2. ESTIMATED REMAINING COAL RESERVES OF THE UNITED STATES, BY RANK, SULFUR CONTENT, AND STATE, ON JANUARY 1, 1965[16,17]

[10^6 short tons][a]

Coal rank and State	Sulfur content, percent									
	0.7 or less	0.8–1.0	1.1–1.5	1.6–2.0	2.1–2.5	2.6–3.0	3.1–3.5	3.6–4.0	Over 4.0	Total
Bituminous coal:										
Alabama	889.2	1,189.3	5,421.7	5,182.8	458.8	417.4	—	—	18.6	13,577.8
Alaska	20,287.4	1,100.0	—	—	—	—	—	—	—	21,387.4
Arkansas	—	—	1,128.4	293.1	154.0	—	40.3	—	—	1,615.8
Colorado	25,178.3	37,237.2	—	—	—	—	—	—	—	62,415.5
Georgia	—	76.0	—	—	—	—	—	—	—	76.0
Illinois [b,c]	—	—	1,808.0	—	1,139.5	17,871.9	36,264.0	62,130.0	20,542.6	139,756.0
Indiana	197.5	173.0	3,645.2	4,248.8	3,543.4	4,110.5	10,872.8	5,105.9	2,944.0	34,841.1
Iowa	—	—	—	—	—	—	117.1	—	6,405.4	6,522.5
Kansas	—	—	519.9	519.7	1,038.7	2,070.6	4,148.0	8,287.3	4,153.8	20,738.0
Kentucky:										
West	—	—	1,119.6	162.0	336.3	3,793.6	12,759.3	13,643.3	5,081.3	36,895.4
East	13,639.9	8,491.9	2,236.8	1,658.8	1,158.3	2,154.4	24.7	—	—	29,414.8
Maryland	—	—	—	124.6	191.8	208.2	378.6	56.4	220.4	1,180.0
Michigan	—	—	—	—	—	—	—	205.0	—	205.0
Missouri	—	—	—	—	—	—	6,456.7	20,669.2	51,634.1	78,760.0
Montana	51.2	218.2	205.0	397.2	400.0	175.0	40.0	27.0	591.0	2,104.6
New Mexico	5,212.0	5,474.0	—	—	—	—	—	—	—	10,686.0
North Carolina	—	—	—	—	—	110.0	—	—	—	110.0
Ohio	—	611.0	369.0	2,110.2	2,750.4	7,810.5	9,785.3	10,148.2	18,439.4	42,024.0
Oklahoma	250.6	772.2	825.0	368.1	—	—	577.2	19.1	490.6	3,302.8
Oregon	—	14.0	—	—	—	—	—	—	—	14.0
Pennsylvania	44.0	1,154.4	7,624.4	12,424.9	19,689.5	9,995.6	5,287.6	1,150.5	580.6	57,951.5
Tennessee	3.3	160.9	715.9	258.7	178.2	190.5	219.7	43.8	68.5	1,839.5
Texas	—	—	—	—	7,978.0	—	—	—	—	7,978.0
Utah	8,551.4	13,584.0	—	1,524.9	—	—	—	—	3,997.7	27,658.0
Virginia	1,981.5	6,077.5	1,637.1	—	123.9	—	—	—	—	9,820.0
Washington	898.9	672.1	—	—	—	—	—	—	—	1,571.0
West Virginia	20,761.0	26,710.6	21,819.7	13,290.6	8,496.1	2,491.8	3,147.4	5,949.2	—	102,666.4
Wyoming	6,222.2	6,596.6	—	—	—	—	—	—	1.1	12,819.9
Other States	—	616.0	—	—	—	—	—	—	—	616.0
Total	104,168.4	110,928.9	49,125.7	42,564.4	47,636.9	51,400.0	90,118.7	127,434.9	105,169.1	728,547.0
Percent of total	14.3	15.2	6.7	5.8	6.5	7.0	12.4	17.5	14.4	100.0

Subbituminous coal:										
Alaska	71,115.6	—	—	—	—	—	—	—	—	71,115.6
Colorado	13,320.8	4,908.7	—	—	—	—	—	—	—	18,229.5
Montana	94,084.4	36,728.0	0.5	1,303.7	—	—	—	—	—	132,116.6
New Mexico	38,735.0	12,000.0	—	—	—	—	—	—	—	50,735.0
Oregon	87.0	87.0	—	—	—	—	—	—	—	174.0
Utah	—	—	150.0	—	—	—	—	—	—	150.0
Washington	3,693.8	500.0	—	—	—	—	—	—	—	4,193.8
Wyoming	35,579.7	72,315.6	—	—	—	—	—	—	8.6	107,903 9
Other States	—	4,047.0	—	—	—	—	—	—	—	4,047.0
Total	256,616.3	130.586.3	150.5	1,303.7	—	—	—	—	8.6	388,665.4
Percent of total	66.0	33.6	0.1	0.3	—	—	—	—	—	100.0
Lignite:										
Alabama	—	—	20.0	—	—	—	—	—	—	20.0
Arkansas	280.0	70.0	—	—	—	—	—	—	—	350.0
Montana	60,214.5	24,141.6	2,660.9	—	—	464.7	—	—	—	87,481.7
North Dakota	284,129.1	34,987.3	31,581.6	—	—	—	—	—	—	350,698.0
South Dakota	—	2,031.0	—	—	—	—	—	—	—	2,031.0
Texas	—	—	6,902.0	—	—	—	—	—	—	6,902.0
Washington	—	116.6	—	—	—	—	—	—	—	116.6
Other States	—	42.0	—	—	—	—	—	—	—	42.0
Total	344,623.6	61,388.5	41,164.5	—	—	464.7	—	—	—	447,641.3
Percent of total	77.0	13.7	9.2	—	—	0.1	—	—	—	100.0
Anthracite:										
Alaska	2,101.0	—	—	—	—	—	—	—	—	2,101.0
Arkansas	—	—	—	145.5	286.3	—	—	—	—	431.8
Colorado	—	90.0	—	—	—	—	—	—	—	90.0
New Mexico	—	6.0	—	—	—	—	—	—	—	6.0
Pennsylvania	12,211.0	—	—	—	—	—	—	—	—	12,211.0
Virginia	335.0	—	—	—	—	—	—	—	—	335.0
Washington	5.0	—	—	—	—	—	—	—	—	5.0
Total	14,652.0	96.0	—	145.5	286.3	—	—	—	—	15,179.8
Percent of total	96.5	0.6	—	0.9	2.0	—	—	—	—	100.0
Grand total	720,060.3	302,999.7	90,440.7	44,013.6	47,923.2	51,864.7	90,118.7	127,434.9	105,177.7	1,580,033.5
Percent of total	45.6	19.2	5.7	2.8	3.0	3.3	5.7	8.0	6.7	100.0

[a] Coal in seams at least 14 inches thick and less than 3000 feet deep in explored areas. Approximately one-half of these reserves are considered recoverable.

[b] See reference 17 for modification of low-sulfur coal reserves for Illinois.

[c] Illinois data are for 1966.

[d] 1967 U.S. Geological Survey estimate differs substantially (23,359 tons).

power generating stations burn subbituminous coal or lignite. Until recently the problems with burning low-rank lignite have kept interest in its use low; however, better firing technology and better equipment have spurred lignite development.[18] Reserves of peat, the first-stage alteration of vegetable matter to coal, are approximately 14,000 million air-dried tons with a heating value of about 5800 to 7900 Btu per pound. Approximately 75 percent of this reserve occurs in Minnesota, Wisconsin, and Michigan.[19]

Approximately two-thirds of the total bituminous reserve is located east of the Mississippi. The economy of mining these reserves has, however, not yet been determined nor is the amount of coal already under contract generally known. The data presented in Table 4-2 indicate that the United States has an abundant supply of coal for many years. However, the availability of low-sulfur coal of high rank is somewhat limited.

4.2.2 Oil

4.2.2.1 Crude Oil—Over the years many estimates have been made of the world's oil reserves. These estimates are based on qualifying assumptions, such as future recovery efficiency and the amount of oil underground still to be found. In this report, the following definitions are used:

1. *Ultimate resources* of crude oil include the sum of past discoveries and estimated reserves that will be discovered in the future.
2. *Proved reserves*[20] include estimated quantities of crude oil that geological and engineering data demonstrate with reasonable certainty to be recoverable in the future from known oil reservoirs under existing economic and operating conditions.
3. *Future recoverable oil reserves* include that remaining portion of the total recoverable reserves, not included in the proved reserves and past production, that present and past production experience suggests can actually be recovered in the future.
4. *Total recoverable reserves* include future recoverable reserves, proved reserves, and past production.

The history of the petroleum industry abounds with estimates of our crude oil reserves. Current estimates of ultimate United States crude-oil reserves are in the range of 500 billion barrels.[4] At the present recovery efficiency, total recoverable reserves for the United States are about 175 billion barrels.

The proved reserves of the United States represent the working inventory of the petroleum industry and have been kept at approximately 31 billion barrels.[11] About 3 billion barrels of domestic crude oil is now being produced per year.[21]

Future recoverable reserves are of major importance since they are based on the present recovery efficiency (approximately one-third) and since they represent the amount of crude oil potentially available in the future. If the recoverability increases in the future, as petroleum authorities project, fu-

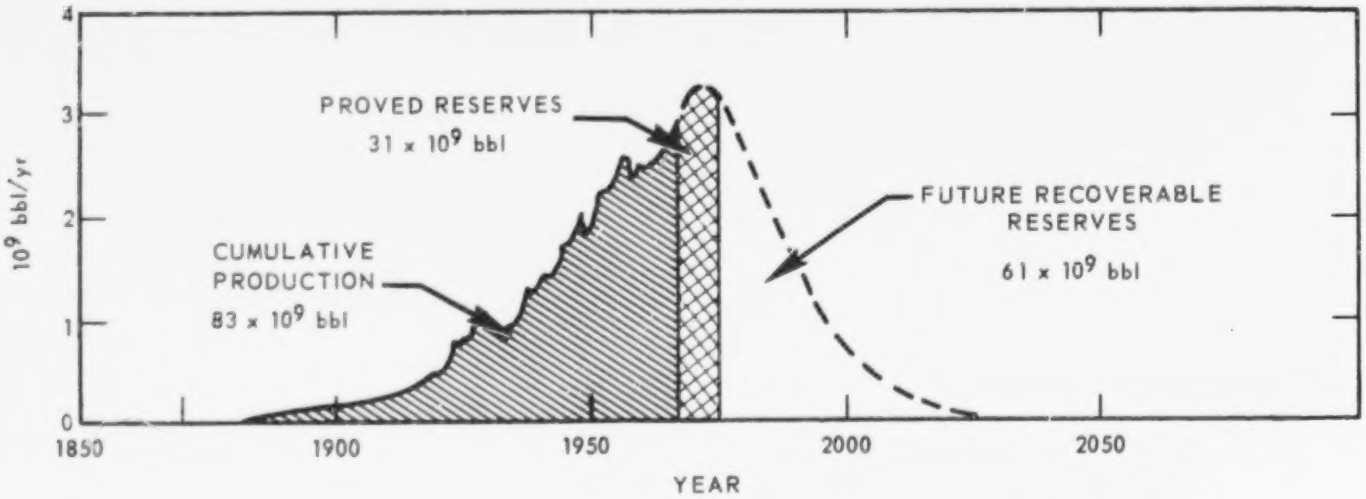

Figure 4-8. Estimate of U. S. production of crude oil as of December 31, 1967.[22]

ture recoverable reserves will increase proportionally.

Since the occurrence of oil, whatever its magnitude, is ultimately finite, exploitation should reach a peak—or perhaps several peaks or an extended plateau—then subside and terminate. Assuming that the estimate of 175 billion barrels of recoverable crude oil for the U.S. is reasonable, the curve in Figure 4–8 should represent the future oil production rate. Of this 175 billion barrels, 83 billion barrels has already been produced. Proved reserves make up another 31 billion barrels, leaving about 61 billion barrels as future recoverable reserves.

Relative price movements, government policy, and changes in the technology of production and distribution have been the key factors in maintaining the continuing upward trend in oil production.

The projected decline in production rate shows that in order to meet the demand, the efficiency of recovery will have to increase, or other sources, such as foreign imports and synthetic crude from oil shale, tar sands, and coal, will eventually become the principal suppliers of crude oil in the United States.

Future additional sources of oil for the United States which appear promising include the potential supplies in the oil shale formations of Wyoming, Colorado, and Utah; the tar sands in Canada and the United States; and the liquefaction of coal[23] (Section 4.4.2.4).

The oil shale formations in the western United States occupy about 16,000 square miles of land.[24] It is estimated that 600 billion barrels of crude oil is recoverable from deposits assaying more than 25 gallons per ton of shale.[25] Plans for the first large commercial plant for extracting and refining this shale into synthetic crude oil at the rate of 58,000 barrels per day have been announced.[25]

It has been known for many years that the Athabasca Tar Sands of Canada are a potential source of oil, but until recently economic extraction from the sand has not been feasible. The first commercially operated plant was dedicated by Great Canadian Oil Sands, Ltd., on September 30, 1967, with a capacity of approximately 45 thousand barrels of synthetic crude oil per day.[26] Most of this crude oil is refined into high-grade distillate products. The ultimate reserves in Canada are estimated to be about 600 billion barrels,[27] 300 billion barrels of which is believed to be recoverable.[26] It is estimated that tar sands recently discovered in Utah contain 46 billion barrels of crude oil in reservoirs favorable to thermal recovery,[29] but the economics of this recovery have not yet been determined.

The distribution of the total United States crude oil production according to sulfur content in 1966 is illustrated in Table 4–3. Al-

Table 4–3. UNITED STATES CRUDE OIL PRODUCTION BY AREA AND SULFUR CONTENT CATEGORY—1966[23]

Area ª	Crude oil production, percent of U.S.	Annual crude oil production, 10^6 bbl					
		Sulfur, weight percent					
		0.00–0.25	0.26–0.50	0.51–1.00	1.01–2.00	2.00	Total
Alaska	0.47	14.3					14.3
Appalachia	0.68	20.4		0.1			20.5
California	11.34	25.7	40.7	110.1	122.5	45.4	344.4
Gulf Coast	29.52	568.4	328.4	0.4			897.2
Illinois, Indiana, Kentucky	3.02	67.3	24.2				91.5
Michigan	0.47	12.0	0.9	1.2	0.1		14.2
Mid-Continent	23.09	215.2	227.9	145.1	79.6	33.8	701.6
Rocky Mountain	9.08	140.4	23.1	47.7	14.0	50.7	275.9
Southeastern U.S.	2.14	13.8	20.0	1.5	7.1	22.5	64.9
West Texas and Southeast New Mexico	20.19	150.2	107.4	90.2	171.3	94.4	613.5
Totals	100.0	1227.7	772.6	396.2	394.6	246.8	3037.9

ª Bureau of Mines Report of Investigations 7059, 1967. Page 3 contains definitions of geographical areas.

most 80 percent of the total has a sulfur content of 1 percent or less by weight.

Significant trends for the period 1956 through 1966 include the following:

1. In the Gulf Coast area a relative increase in production of crude oil containing 0.26 to 0.50 percent sulfur.
2. In the Mid-Continent area a decrease in production of crude oil in the 0.26 to 0.50 percent sulfur category.
3. In the Rocky Mountain area an increase in production of crude oil in the 0.00 to 0.25 percent sulfur category.

The distribution for 1966 of the foreign crude oil production within the free world, excluding the United States, is shown by area and sulfur content in Table 4–4. The percentage distribution in each sulfur content category is included. Note that the majority of crude oil containing less than 1.0 percent sulfur is located in Africa and Canada.

Data on the crude oil imported into the United States in 1966 are summarized in Table 4–5. The average sulfur content of these imports may be approximated on the basis of the average sulfur contents shown in Table 4–4. These imports account for about 15 percent of United States production.

Table 4–4. FOREIGN CRUDE OIL PRODUCTION BY AREA AND SULFUR CONTENT CATEGORY[27]

Area and sulfur content range, weight percent	1966 production	
	10^6 bbl	Percent
Africa:		
0.00–0.25	637	63.7
0.26–0.50	144	14.4
0.51–1.00	216	21.6
1.01–2.00	—	—
>2.00	3	0.3
Canada:		
0.00–0.25	112	35.4
0.26–0.50	18	5.7
0.51–1.00	107	33.7
1.01–2.00	40	12.6
>2.00	40	12.6
Middle East:		
0.00–0.25	—	—
0.26–0.50	—	—
0.51–1.00	—	—
1.01–2.00	1509	44.8
>2.00	1862	55.2
South America:		
0.00–0.25	24	1.6
0.26–0.50	19	1.3
0.51–1.00	52	3.5
1.01–2.00	225	15.2
>2.00	1161	78.4

The President of the United States, under Section 232 of the Trade Expansion Act of 1962, may make adjustments in the imports of crude oil, unfinished oils, and finished products as necessary so that such imports do not threaten our national security. For instance, Proclamation 3894 Federal Register, Vol. 32, No. 138, July 19, 1967, in support of Federal, State, and local rules and regulations for air pollution control, allowed the petroleum industry to provide additional supplies of low-sulfur residual fuel oil to the fuel combustion market.

All allocations or licenses to import crude oil, unfinished oils, or finished products are granted according to regulations of the Oil Import Administration, Department of the Interior, under review of the Secretary. Such allocations may become even more important in the future with the expected increased demand for low-sulfur fuels.

Table 4–5. CRUDE OIL IMPORTED INTO UNITED STATES—1966[28]

(10^6 bbl)

Area	Amount
North America	126.7
South America	163.1
Middle East	107.6
Africa	31.5
Asiatic Areas	18.2 [a]
Total	447.1

[a] Sumatra crude oil imported into West Coast—sulfur content, by weight, is 0.1 percent.[29]

Regulations liberalizing the importation of low-sulfur crude oils to permit production of low-sulfur fuel oils have already been established for the West Coast by the Department of the Interior, and similar changes are being considered for the East Coast.

4.2.2.2 Residual Fuel Oil—Refining of crude oil produces various grades of fuel oil in addition to other lighter petroleum products such as gasoline. Due to the nature of the refining processes, and the characteristics of the sulfur compounds in crude oil, the sulfur is concentrated in the heavier fractions, which have higher boiling points.[30]

The American Society for Testing and Materials (ASTM) in its publication "D396—

Standard Specifications for Fuel Oils," classifies fuel oils into two main categories—distillates and residuals. These in turn are then subdivided into five grades, 1, 2, 4, 5, and 6. There are three commercial grades of residual oil marketed in the United States—grades 4*, 5, and 6. Grades 4 and 5 are produced either as straight-run fractions, or by blending grades 6 and 2. They are used primarily for heating commercial and industrial buildings. Grade 6 is described as a heavy oil, and is used extensively to fire large boilers in public utility, industrial, and commercial installations; and as a fuel for large diesel engines, especially marine engines.[11] In marine applications, grade 6 is often referred to as bunker fuel oil, or Bunker C. The average sulfur content of these three grades range from 0.5 to 5.0 percent by weight with the majority in the range of 0.75 to 2.5 percent.

Currently, about 7 percent of domestic crude oil ends up as residual oil fractions, compared to 14 percent in 1957.[4] The distribution by region and by sulfur content of residual oil from domestic crude is shown in Table 4–6. This fuel is substantially all committed and delivered to specific markets, such as the metal industry. This being the present trend, imported residual fuel oil, higher in sulfur content, has become the principal source of other major consumer groups. South American countries, due to factors such as water transportation, have become the chief suppliers of this product (as indicated in Table 4–7), supplying over 90 percent of the residual fuel oil imported during the period 1964 through 1966. The average sulfur content of this South American residual oil is 2.25 percent by weight. The total 376,795,000 barrels of imported residual oil constitutes over 61 percent of the total domestic consumption of this fuel in 1966. The other 39 percent originated from foreign and domestic crudes refined in the United States.

The total consumption of residual oil by major consuming groups in the United States is illustrated in Table 4–8 for the years 1963 through 1966. By 1966, the eastern States consumed 420 million barrels, the western States about 100 million barrels, and the gulf coast and inland States about 100 million barrels.[3]

The sulfur oxide emissions that result from the combustion of this tremendous volume of high-sulfur fuel have presented a problem for some large cities. Air pollution control legislation now in force in some of these cities limits the sulfur content of fuels burned, resulting in an increased demand for low-sulfur fuel.

The Secretary of the Interior, in an attempt to help alleviate the problem of importing high-sulfur residual oils, announced on July 17, 1967, a modification of the oil import program. In essence, the definition of residual

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* Grade 4 is actually a blend of distillate and residual fuels, and is currently classified as a residual fuel oil for import purposes.

Table 4–6. RESIDUAL FUEL OIL PRODUCTION FROM DOMESTIC CRUDE OIL IN U.S. BY SULFUR CONTENT[a]—1965[32,33]

[10³ bbl]

Sulfur, percent	East Coast	Gulf States	Central States	Pacific Coast	Total	Percent of total
<0.7		3,310	8,750	1,975	14,035	7.9
0.7–1.0	930	4,728	12,920	8,138	26,716	15.0
1.0–1.5		15,472	19,250	5,186	39,908	22.5
1.5–2.0	2,200	4,000	200	24,575	30,975	17.5
2.0–3.0	15,650	9,360	25,518	6,600	57,128	32.0
>3.0		2,200	2,110	4,300	8,610	4.9
Regional total	18,780	39,070	68,748	50,774	177,372	100.0
Regional percent	10.6	22.0	38.3	28.6	100	
Average S percent	2.44	1.61	1.70	1.72	1.76	

[a] 99 percent of the operating refineries.

fuel oil was broadened to include grade 4 fuel oil, which had previously been considered distillate. This fuel usually has a sulfur content of under 1.5 percent. The definition of residual fuel oil also was expanded to include those low-sulfur crude oils that may be burned directly as fuel oil without any processing. Thus, low-sulfur fuel from two new sources now is available to users of residual fuel oil.

4.2.2.3 Distillate Fuel Oil—Distillate fuel oils, grades 1 and 2, are principally used for heating homes, domestic hot water, small apartment houses, and in certain industrial processes where simplified burning apparatus is required and the firing rate is usually not more than 20 to 25 gallons per hour.[34] These distillate oils normally have a heating value of 5.8 to 6 million Btu per barrel. The average sulfur content of this fuel is between 0.04 and 0.35 percent by weight. Table 4–9 gives a breakdown, by section of the country, of the average sulfur content of grades 1 and 2. Because of the relatively low sulfur content, distillate fuel oils can be burned without creating large amounts of sulfur oxide emissions.

Quantities of distillate fuels for various user categories have been reported and show

Table 4–7. RESIDUAL FUEL OIL IMPORTS INTO UNITED STATES 1964–1966[33]

Country of origin	Imports, 10^3 bbl			1966 average sulfur, percent
	1964	1965	1966 [a]	
Venezuela	142,256	180,538	194,676	2.2
Netherlands Antilles (Aruba, Curacao)	95,182	103,645	100,101	2.46
British West Indies (Trinidad and Tobago)	36,527	37,600	44,614	1.93
Mexico	6,684	5,839	6,067	4.4
Italy	12	422	5,264	2.8
Puerto Rico	4,787	4,371	4,749	2.2
Argentina	1,290	2,945	4,346	1.0
Colombia	1,485	3,090	3,515	1.55
England	—	95	2,109	3.5
Canada	1,826	1,964	1,880	2.65
Netherlands	117	41	1,285	3.00 [b]
Panama	1,541	1,231	1,113	2.00 [b]
Kuwait	—	—	1,093	—
Others	4,184	3,406	5,983	—
Totals	295,891	345,187	376,795	—

[a] Preliminary.

[b] Estimated.

Table 4–8. TOTAL U.S. CONSUMPTION OF RESIDUAL OIL BY MAJOR CONSUMING GROUP—1963–1966[a]

[10^3 bbl]

Consuming group	1963	1964	1965	1966
Heating oils (apartments and commercial)	125,248	126,215	156,254	167,471
Industrial (excluding oil company fuel)	149,269	157,176	140,602	141,050
Oil company use (excluding heating oil)	46,976	43,098	34,354	35,177
Electric generation utilities	91,615	97,595	114,884	140,642
Railroads	5,342	5,350	4,001	3,792
Bunkering of vessels (excluding military)	76,502	83,024	73,639	73,641
Military use	36,444	35,568	40,380	41,861
Miscellaneous	7,126	8,606	10,004	10,338
Totals	538,522	556,632	574,118	613,972 [a]

[a] 376,795,000 barrels were imported.

Table 4–9. AVERAGE SULFUR CONTENT OF DISTILLATE FUEL OILS FOR UNITED STATES BY REGION [a]—1967 [36]

Region	Grade	
	No. 1	No. 2
Eastern	0.060	0.232
Southern	0.040	0.184
Central	0.089	0.283
Rocky Mountains	0.105	0.321
Western	0.124	0.307

[a] Region boundaries defined in reference 36.

that about 85 percent of all distillate fuels other than diesel fuel and kerosene is used for space heating. In 1966, about 506 million barrels of distillate fuel, excluding diesel fuel, was consumed.[35]

4.2.3 Natural Gas

Natural gas is a mixture of low-molecular-weight hydrocarbons. Methane is almost always the major constituent. It ordinarily has a negligible sulfur content; however, if the sulfur content is significant in its natural form the gas must be processed to reduce the sulfur compounds before it can be marketed. Natural gas occurs underground either dissolved in oil, in reservoirs of gas above pools of oil, or in gas fields unassociated with oil.

The allocation of this fuel and its cost when it is shipped interstate are the responsibility of the Federal Power Commission. Such factors as potential supply, reserve-production ratio, present and future technologies available to improve recovery and economic factors, and improvement in methods of production of a comparable synthetic will influence these decisions.

Most of the gas produced in the United States has come from reservoirs without oil, or in areas where the production of gas is not significantly affected by the oil.[37] Figure 4–9 outlines the location of these fields throughout the United States. Authoritative annual estimates of proved reserves of natural gas* in the United States and estimated yearly production figures have been prepared since 1946 by the Committee on Natural Gas Reserves of the American Gas Association.

Natural gas reserves in the United States will be covered under two general headings—proved reserves and potential supply. The potential supply is divided into three categories—probable, possible, and speculative. (See reference 38, for definitions of these terms). Total recoverable reserves include the total of proved reserves and potential supply of natural gas.

The proved recoverable reserves (at 14.73 psia and 60°F) in the United States as of December 31, 1967, were 292.9 trillion cubic feet, while the total potential supply was estimated to be 690 trillion cubic feet, resulting in a total recoverable reserve of about 983 trillion cubic feet.[38, 39] The proved reserves by State are shown in Table 4–10. About 70 percent of the potential supply of natural gas is located in the south-central and gulf coast States.

Proved reserves have continued to increase through 1967, although at a slightly reduced rate. This reduction is attributed to the fact that the rate of consumption has been increasing over the past few years while the rate of development of new fields has remained relatively constant. Since 1946, when the American Gas Association first initiated its annual proved reserves study, about 146 trillion cubic feet of natural gas has been added to the proved reserves, while the actual annual production has increased from 4.9 trillion cubic feet in 1946 to 18.4 trillion cubic feet in 1967.[40]

Within the next few years, production of natural gas for the first time will probably exceed the new supply developed. If past trends continue, total proved reserves may peak at approximately 300 trillion cubic feet in 1971 or 1972; and, if projections are right, reserves will decrease to about 273 trillion cubic feet by 1980.[41] It is estimated that net production will rise from 18.4 trillion cubic feet in 1967 to 20.5 trillion cubic feet in 1970, 24.25 trillion cubic feet in 1975, and 27.0

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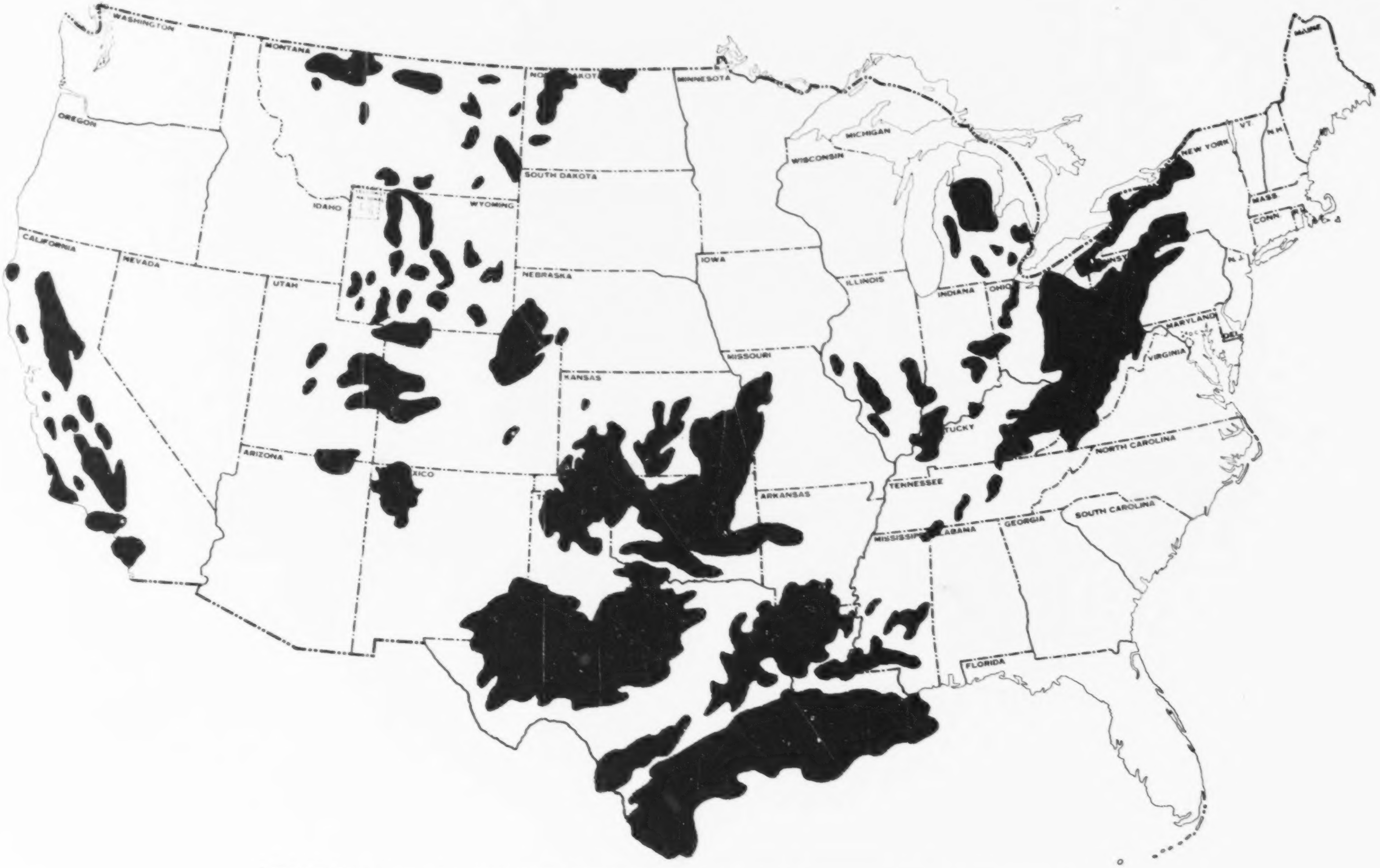
* Proved reserves of natural gas, as used by the American Gas Association Committee of Natural Gas Reserves, means the current estimated quantity of natural gas and natural gas liquids which analysis of geologic and engineering data demonstrates with reasonable certainty to be recoverable in the future from known oil and gas reservoirs under existing economic and operating conditions.


WASHINGTON
OREGON
CALIFORNIA
NEVADA
IDAHO
MONTANA
WYOMING
UTAH
ARIZONA
SOUTH DAKOTA
NEBRASKA
KANSAS
MINNESOTA
IOWA
MISSOURI
ARKANSAS
WISCONSIN
MICHIGAN
ILLINOIS
INDIANA
OHIO
TENNESSEE
MISSISSIPPI
GEORGIA
SOUTH CAROLINA
NORTH CAROLINA
VIRGINIA
MARYLAND
DEL
N.J.
NEW YORK
VT
N.H.
MAINE
MASS
CONN
FLORIDA

LOCATION OF FIELDS OUTLINED FROM FEDERAL POWER COMMISSION MAP AS OF JUNE 30, 1966.

Figure 4-9. Natural gas fields of the United States.

Table 4–10. ESTIMATED PROVED RECOVERABLE RESERVES OF NATURAL GAS IN UNITED STATES [39, 40]

[10^6 ft^3—14.73 psia, at 60° F]

State	As of Dec. 31, 1966	As of Dec. 31, 1967
Alaska	2,946,862	3,635,254
Arkansas	2,599,629	2,811,251
California [a]	8,474,393	7,723,797
Colorado	1,651,406	1,769,263
Illinois	236,493	258,604
Indiana	71,207	74,781
Kansas	15,923,275	15,283,657
Kentucky	1,017,007	953,983
Louisiana [a]	83,684,092	86,290,009
Michigan	773,131	760,912
Mississippi	1,668,863	1,597,007
Montana	620,350	837,718
Nebraska	72,757	63,792
New Mexico	14,753,142	15,092,465
New York	120,871	121,086
North Dakota	1,024,509	882,132
Ohio	755,215	762,731
Oklahoma	20,122,191	19,403,806
Pennsylvania	1,350,576	1,392,170
Texas [a]	123,609,326	125,415,064
Utah	1,372,225	1,226,517
Virginia	37,586	37,798
West Virginia	2,622,237	2,579,986
Wyoming	3,594,046	3,685,459
Miscellaneous [b]	231,416	238,461
Total U.S.	289,332,805	292,907,703

[a] Includes offshore reserves.

[b] Includes Alabama, Arizona, Florida, Iowa, Maryland, Missouri, Tennessee, and Washington.

trillion cubic feet in 1980. Marginal reservoirs of natural gas may become economically recoverable by such treatments as the use of underground nuclear exposions.[42]

There are three major classes of natural gas consumers: residential, commercial, and industrial. Almost without exception, residential and commercial customers are served by public utilities, whereas industrial customers are served by distributors and pipeline companies. Table 4–11 shows natural gas consumption by principal use in the United States. Industrial customers use about two-thirds of all natural gas in the United States, and residential customers use about one-fourth.

Gas is supplied on either a continuous or an interruptible basis. Continuous service provides the consumer with gas according to his needs; interruptible service is provided only when the distribution system has sufficient gas. Usually, residential and commercial service is on a continuous basis but large users may be served on an interruptible basis. Thus, when there is a heavy demand from the residential and commercial categories, it may be necessary for large industries to switch to another fuel.

4.2.3.1 Other Sources of Natural Gas—Importation of natural gas at the present time is limited to small shipments by pipeline from Canada and Mexico. Net imports from Canada—less than 3 percent of United States

Table 4–11. NUMBER OF CUSTOMERS [a] AND VOLUME OF NATURAL GAS CONSUMED BY PRINCIPAL USERS IN THE UNITED STATES [3]

Region	Number of customers, in thousands		Volume of natural gas, 10^6 ft^3			
	Residential	Commercial	Residential	Commercial	Industrial	Total consumption
New England	1,532	102	103,867	29,662	52,615	186,144
Middle Atlantic	7,490	563	721,653	214,180	600,357	1,536,190
East North Central	8,181	642	1,281,536	469,760	1,292,063	3,043,339
West North Central	3,001	334	452,154	220,794	958,174	1,631,122
South Atlantic	3,005	265	281,628	111,727	676,468	1,069,823
East South Central	1,679	163	172,489	97,742	635,674	905,905
West South Central	4,081	435	382,259	174,189	5,197,153	5,753,601
Mountain	1,580	172	211,507	111,858	664,568	987,933
Pacific	5,535	444	531,166	192,828	1,353,640	2,077,634
Total United States:						
1966	36,084	3,120	4,138,259	1,622,740	11,430,712	17,191,711
1965	35,302	2,991	3,902,802	1,443,648	10,686,739	16,033,189

[a] Based on number of installed meters.

consumption—are expected to rise rapidly, from 482 billion cubic feet in 1967 to 1350 billion cubic feet in 1980.[41] Net imports from Canada and Mexico should rise to 3.8 percent of the United States demand by 1970 and to as much as 5.1 percent in 1980.[41]

A third promising source of imports is shipment by tanker of natural gas in liquid form from countries such as Venezuela. This source is technically feasible and the economics of importation is being studied at the present time. The Philadelphia Gas Works is currently constructing a liquified natural gas plan to handle its peaking load and plans to start importing liquified natural gas in 3 to 5 years.[43]

4.2.3.2 Natural-Gas Liquids—Natural-gas liquids are byproducts resulting from production of natural gas. The ratio of natural gas to natural-gas liquids is approximately 30,000 cubic feet of gas per barrel of liquids. It is estimated that total proved reserves of about 8.6×10^9 barrels of natural-gas liquids exist in the United States.[39]

The 1966 net production of natural-gas liquids was approximately 588×10^6 barrels.[39] Of this total, liquid-petroleum gases and ethane accounted for about 61 percent, natural gasoline and isopentane for about 29 percent, other products for about 8 percent, and finished gasoline and naphtha for 3 percent.[3] Combustion of these fuels produces very little sulfur oxide emission.

4.2.4 Hydroelectric Power

Hydroelectric power does not require fuel for generation and, therefore, does not create any sulfur oxides. Hydroelectric generation presently accounts for 18 percent of the electrical energy produced in the United States, but it is estimated that by 1980 only 13 percent of the total electrical energy will be supplied by this source. Figure 4–10 and Table 4–12 show the locations and trends for hydroelectric projects.

Table 4–12. EXISTING AND PROJECTED HYDROELECTRIC CAPACITY OF UNITED STATES TO 1980[45]

	10^6 kw
Existing capacity	45.8
Capacity under construction	14.6
Subtotal 1970	60.4
Estimated additions to 1980	17.6
Total 1980	78.0

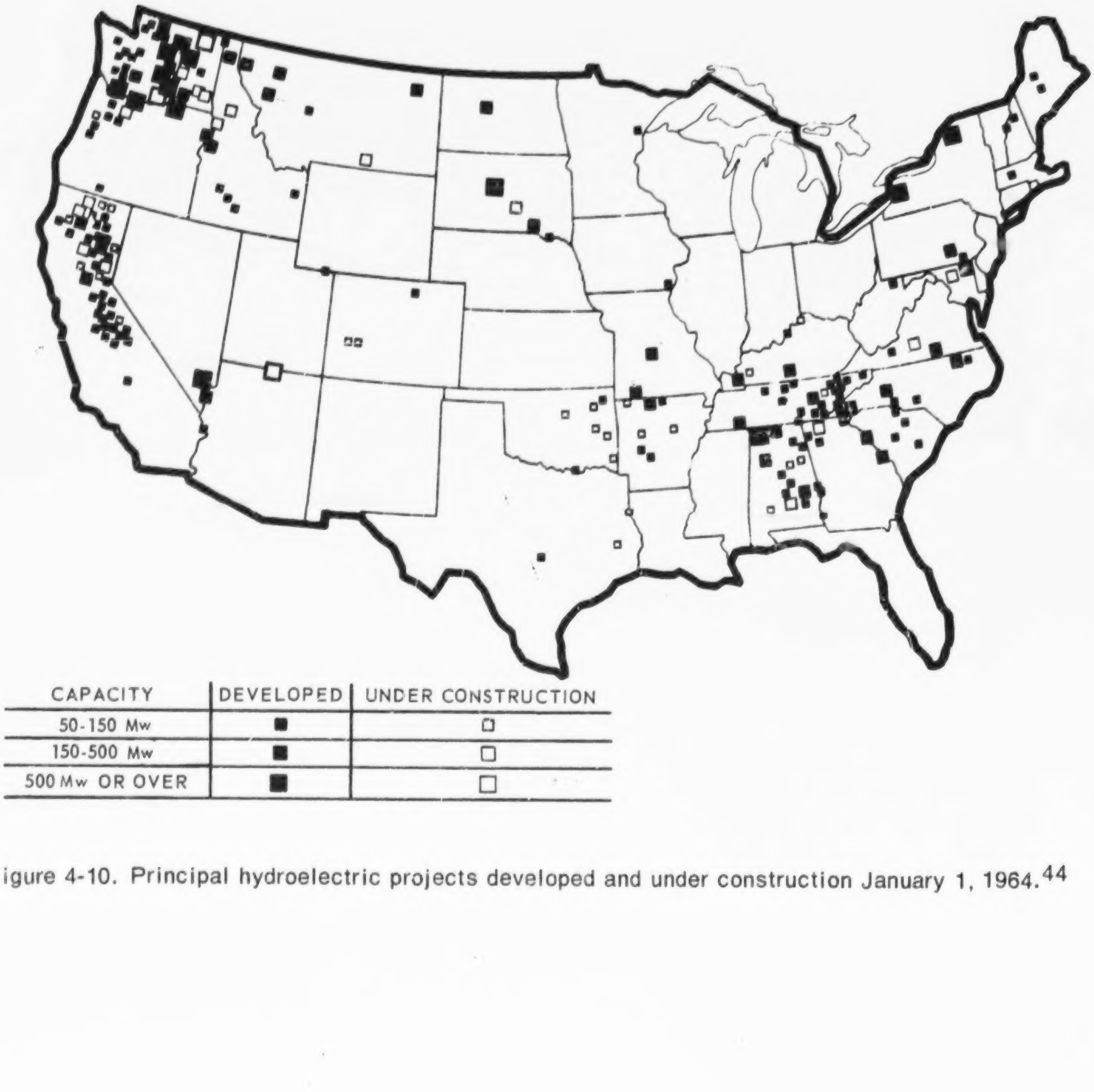
4.2.5 Nuclear Power

The utility industry in the United States has accepted nuclear power as a safe, reliable, and economic means of meeting a large proportion of its new requirements for generating capacity. By the end of 1968 about 90 nuclear plants totaling approximately 65 million kilowatts of electrical generating capacity were on order, under construction, or operable.[49] The utility industry has committed over 11 billion dollars to nuclear plant capital investments (including initial fuel) and lifetime power costs from nuclear plants now committed will approach 50 billion dollars. Whereas, approximately 1% of the electrical generating capability today is nuclear, it is estimated that 23 to 30% will be nuclear in 1980 and about 50% in 2000.

Economies of scale prevail for all types of steam-electric generating units, but are most pronounced for nuclear plants, as is illustrated by the fact that 22 of the nuclear plants presently committed exceed 1 million kilowatts of electric generating capacity.

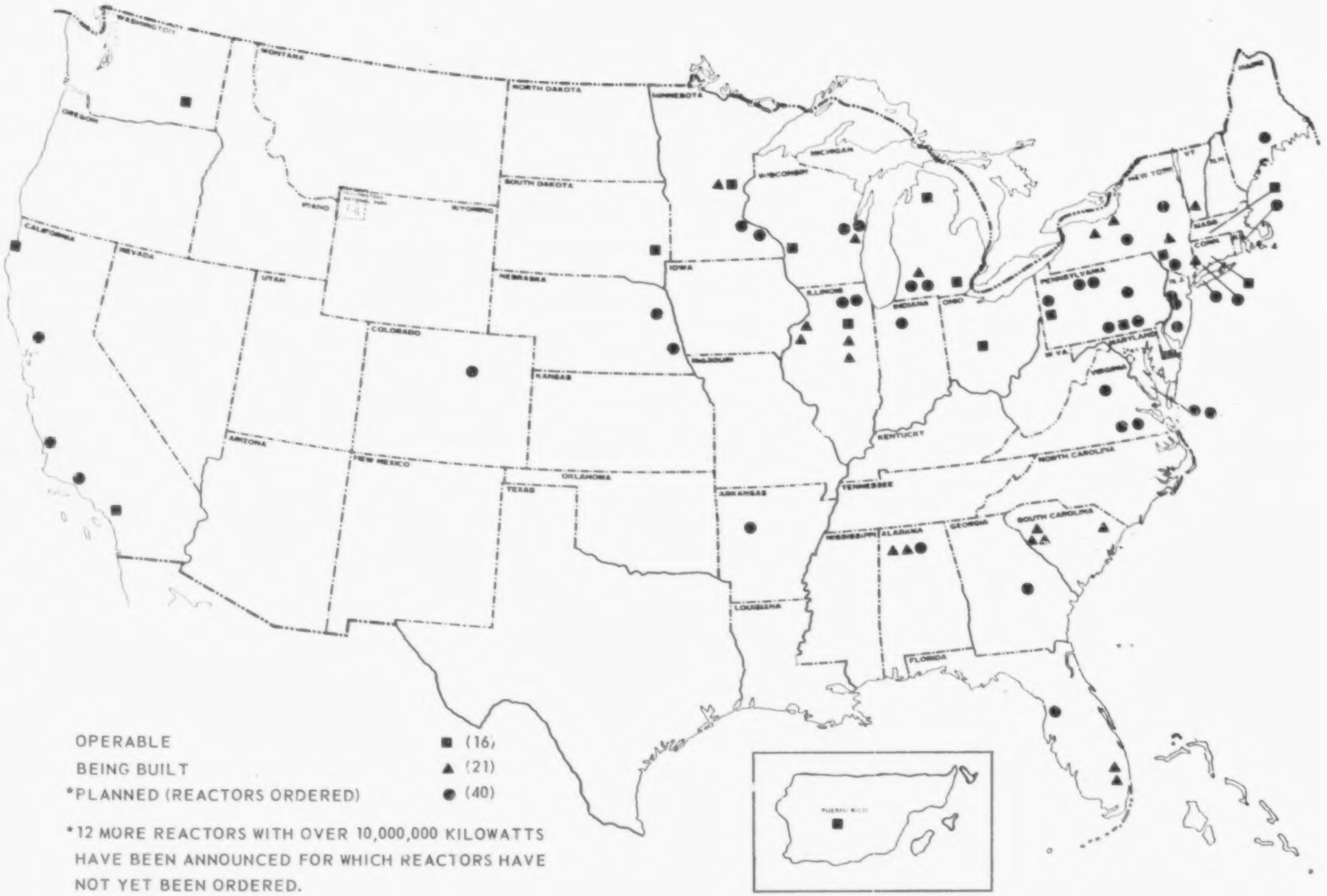
Present-day power reactors utilize only a small fraction of the nuclear raw material. In view of this and the rapid increase in the projected requirements for uranium, some concern has been expressed as to whether a sufficient amount of material can be obtained to meet these requirements. Known reserves are sufficient to fuel the projected nuclear capacity through the late 1970's, and a rapid expansion of private drilling activity is under way.[19, 37, 44, 46, 52, 53] Within the next year or so considerably more information, available as a result of these accelerated exploratory efforts, should permit better assessment of the future prospects for the development of additional sources of uranium.[22, 37, 46, 50, 51]

To enable more efficient use of the nuclear raw material, intensive development of fast breeder reactors (which create more fissionable material than they consume) is being undertaken by the Atomic Energy Commission and by private industry. The energy



CAPACITY	DEVELOPED	UNDER CONSTRUCTION
50-150 Mw	■	□
150-500 Mw	■	□
500 Mw OR OVER	■	□

Figure 4-10. Principal hydroelectric projects developed and under construction January 1, 1964.[44]



OPERABLE ■ (16)
BEING BUILT ▲ (21)
*PLANNED (REACTORS ORDERED) ● (40)

*12 MORE REACTORS WITH OVER 10,000,000 KILOWATTS HAVE BEEN ANNOUNCED FOR WHICH REACTORS HAVE NOT YET BEEN ORDERED.

Figure 4-11. Status of nuclear power plants in the United States as of December 31, 1967.[49]

that can be extracted from the low-cost ores will thereby be extended by factors of 10 to 30. The relative insensitivity of breeder reactors to ore prices will also make useable the large amounts of uranium available from higher cost ores.

The light water-cooled nuclear reactors used in the commercial power plants currently accepted by the utility industry operate at a lower thermal efficiency than modern fossil fuel plants. This results in increased waste heat and an increase in cooling water requirements. The trend towards larger power plant size coupled with an increase in demand for cooling water is a complicating factor in power plant siting. The advanced reactors now under development should have efficiencies comparable to fossil plants.

The potential of nuclear power plants to contaminate the environment with radioactivity under emergency conditions is recognized and provisions must be made to assure maintenance of the health and safety of the public.[47] Disposal of radioactive wastes from spent nuclear fuel is effectively accomplished by shipping the used fuel element intact to remote chemical processing facilities for recovery of the unused nuclear fuel and disposal of the radioactive wastes. The utilization of nuclear power in highly populated areas will depend upon the accumulation of nuclear power experience and the continuing development and demonstration of the effectiveness of engineering safeguards.[47]

The future requirements of electrical energy and the trends in recent years with regard to power plant sizes place greater emphasis on the environmental problems of plant location. The requirements with regard to air and water quality control and aesthetics result in increased restraints on the selection of plant sites, especially those located near load centers.

Nuclear power offers a means of providing access to virtually limitless sources of electricity at low cost for all areas of the country, including those areas which have been denied low-cost power because of distance from fossil fuel sources or hydro resources. The use of nuclear power plants will result in virtual elimination of air pollution from electrical power plants and provide other aesthetic and environmental benefits by such inherent features as reduced acreage requirements, elimination of tall stacks, and areas for coal handling storage facilities, ash disposal, and railroad switch yards.

4.2.6 Other Energy Sources

Although it is expected that the United States will continue to derive the major portion of its energy from fossil fuels, nuclear energy, and hydroelectric power, there are several other energy sources worth mentioning because they produce no SO_2 emissions.

Solar energy is a continuous and inexhaustible source of power. The total amount of power that the earth receives as radiation from the sun is approximately 5×10^{17} Btu per hour,[54] which far exceeds the amount of power that can be generated from fossil fuels. The application of solar power in the United States has been very limited, due largely to technical and economic problems of conversion. This trend is not expected to change in the near future.[55]

Reserviors of *geothermal heat* underlie the volcanic regions of the earth. The heat can be withdrawn and used either in the form of hot water or steam under pressure. In the United States, the Pacific Gas and Electric Company has had geothermal plants in operation since 1959 and they will soon build a 55-megawatt unit.[56] The availability of geothermal heat in the United States is limited to the western part.

Heat-reclaim systems utilize the excess heat generated in one area to heat another area which is deficient in heat. This type of system has been utilized in some large buildings for several years. A recent announcement says that school buildings will be heated by the excess heat generated by the 1300 students (450 Btu per hour each) and by lighting, cooking, and other incidental interior sources.[57] The absence of additional fuel combustion for heating purposes results in a net reduction on emissions of sulfur dioxide from this source.

Fuel cells are electrochemical devices that produce electricity through direct conversion of chemical energy. Fuel cells differ from batteries in two major respects: they operate continuously as long as fuel and oxidizer are supplied from an external source, and the electrolyte remains chemically unchanged, that is, it need not be recharged.

The application of fuel cells has to date been limited to space research and military uses because of the high initial cost. Providing energy to transportation vehicles is a possible future application. Widespread application will, however, depend on technological advances sufficient to reduce initial cost and permit the use of low-cost fuels. Some experts feel that sufficient information is already available to design a large-scale power plant using a high-temperature cell with coal as a fuel.[59]

Although heat produced during the incineration of refuse is usually wasted, it could be used to produce steam, which would have many applications. The heating value of mixed refuse today averages about 4500 to 5000 Btu per pound. This value can be expected to increase because the trend is toward less garbage and more paper and plastics. The sulfur content of refuse is approximately 0.1 percent, therefore, the emission of sulfur dioxide from refuse incineration is of minor importance.[60]

4.3 ENERGY SOURCE SUBSTITUTION

4.3.1 Introduction

Substitution of energy sources with little or no potential sulfur oxide emissions for high-sulfur sources is one of the best methods presently available for reducing sulfur oxide emissions. Thus, conversion to nuclear fuel or hydropower for electrical generation, or substituting fuels low in sulfur such as gas, or low-sulfur coal or oil for high-sulfur fuels can greatly reduce sulfur oxide emissions. Reduction of particulate emissions is another benefit to be derived from using some low-sulfur fuels. Simultaneous reduction of two pollutants (sulfur oxides and particulates) is a very desirable and important feature of fuel substitution.

The major arguments against this means of control are that adequate quantities of low-sulfur fuel are not available at an economical price and changing the fuel-use patterns would disrupt the fuel market. A drastic change in fuel-use patterns could result in a shortage of low-sulfur fuels.

The fuel and transportation price structure in the United States is very complex and there are many factors involved in determining the ultimate price of a fuel. Fuel rates vary widely, depending on factors such as geographical location, user category, and quantity required.

Costs, in 1967, of fossil fuels in various parts of the country are presented in Tables 4–13, 4–14, and 4–15. These are prices of fuels delivered to industrial consumers with heat input requirements greater than 5 billion Btu per hour. These consumers receive fuel in bulk quantity, their fuel costs reflecting bulk quantity delivery. Fuel costs for public utility steam-generating plants are contracted separately at each installation; these costs have been well documented and are, therefore, not included in this tabulation.[61]

The prices in Table 4–13 are for coal from the nearest producing district (f.o.b. mine price). In addition, prices of District 7 and 8 coals for each Standard Metropolitan Statistical Area (SMSA) are determined. Coals from Districts 7 and 8 are low-sulfur fuels, in the 0 to 0.7 percent and 0.8 to 1.4 percent sulfur range. Table 4–16 shows the producing districts and mine prices.

4.3.2 Methodology and Economics of Fuel Substitution

A number of alternatives are available for switching from high-sulfur fuel to a low-sulfur fuel. Typical examples include switching from:

1. High-sulfur coal to low-sulfur coal.
2. High-sulfur coal to low-sulfur residual oil.
3. High-sulfur residual oil to low-sulfur residual oil.
4. Sulfur-bearing fuel to gas.

All the logical possibilities of fuel substitution to reduce sulfur emissions are shown in Figure 4–12. Electric heating, although considered a substitute energy in some circumstances, is generally only a relocation of the sulfur oxide emissions and is not considered here. In some cases, however, the electricity

Table 4-13. INDUSTRIAL CONSUMER PRICES OF COAL—1967

[Cents/10⁶ Btu]

Destination	Sulfur ranges, weight percent			
	<0.7	0.8-0.9	1.8-2.0	2.9-3.7
Hartford, Conn.	45-48	41-49	35-43	[a]
Boston, Mass.	48-49	44-50	36-45	—
Providence-Pawtucket-Warwick, R.I.—Mass.	45-48	41-49	36-45	—
Buffalo, N.Y.	41-43	34-49	30-36	—
New York, N.Y.	40-42	38-46	34-41	—
Syracuse, N.Y.	—	39-47	32-30	—
Allentown-Bethlehem-Easton, Pa.—N.J.	41-43	37-43	32-40	—
Philadelphia, Pa.	41-43	37-43	32-38	—
Pittsburgh, Pa.	39-41	34-40	27-39	—
Wilmington, Del.-N.J.—Md.	41-43	37-45	32-39	—
Washington, D.C.-Md.—Va.	38-47	34-41	32-39	—
Jacksonville, Fla.	42-45	37-43	—	39-41
Miami, Fla.	47-50	41-49	—	44-47
Atlanta, Ga.	41-44	36-39	—	32-34
Baltimore, Md.	40-43	35-42	31-38	—
Norfolk-Portsmouth, Va.	37-39	33-39	—	—
Charleston, W. Va.	30-31	24-25	—	—
Huntington, W. Va.	32-33	27-27	—	—
Chicago, Ill.	40-43	34-41	—	27-34
Gary-Hammond-E. Chicago, Ind.	40-43	34-41	—	31-32
Indianapolis, Ind.	38-40	32-38	—	26-29
Detroit, Mich.	38-41	32-39	—	30-35
Flint, Mich.	39-42	33-40	—	32-37
Akron, Ohio	38-40	31-38	—	—
Cincinnati, Ohio-Ky.—Ind.	33-36	27-33	37-45	28-30
Cleveland, Ohio	38-40	31-38	—	26-29
Steubenville-Wierton, Ohio—W. Va.	38-40	31-38	—	26-29
Toledo, Ohio—Mich.	38-38	31-35	—	27-31
Milwaukee, Wisc.	42-45	36-44	—	33-38
Birmingham, Ala.	40-41	34-40	—	32-34
Louisville, Ky.—Ind.	35-37	29-33	—	21-22
Chattanooga, Tenn.—Ga.	38-39	33-38	—	31-33
Memphis, Tenn.—Ark.	41-44	36-43	—	28-28
Davenport-Rock Island-Moline, Iowa—Ill.	42-68	37-45	—	32-37
Kansas City, Mo.—Kan.	48-51	42-51	—	37-43
Minneapolis-St. Paul, Minn.	42-63	42-51	—	33-39
St. Louis, Mo.—Ill.	40-43	34-41	—	25-30
Omaha, Nebr.—Iowa	42-63	42-51	—	38-46
Oklahoma City, Okla.	—	—	46-46	—
Denver, Colo.	30-60	—	—	—
Salt Lake City, Utah	40-69	38-72	—	—
Los Angeles-Long Beach, Calif.	55-74	55-77	—	—
San Francisco-Oakland, Calif.	57-74	55-77	—	—
Portland, Ore.—Wash.	52-74	51-77	—	—
Seattle, Wash.	53-74	52-77	—	—

[a] Dash (—) indicates data on coal prices not available.

may be produced by a noncombustion process, thus eliminating emissions.

A study of the economics of energy source substitution includes the incremental fuel costs and capital investment requirements for boiler modification to accept a fuel substitute. While not considered in the following cost analysis because of their variability, plant down-time and loss of capacity during boiler modification may be added cost items.

Capital investment is the cost of modifying a boiler unit to facilitate the combustion of

Table 4-14. INDUSTRIAL CONSUMER PRICES OF FUEL OILS—1967

[Cents/10^6 Btu]

Standard Metropolitan Statistical Area SMSA	Fuel oil category						
	No. 1	No. 2	No. 4	No. 5 No S guar	No. 5 1 percent S guar	No. 6 No S guar	No. 6 1 per cent S guar
Hartford, Conn	(a)	—	—	—	—	43	—
Boston, Mass	95	84	58	52	—	37	—
Providence-Pawtucket-Warwick, R.I.—Mass	95	84	55	52	—	38	—
Buffalo, N.Y	—	87	—	—	59	50	54
New York, N.Y	94	83	53	45	—	37	48
Syracuse, N.Y	—	—	—	—	—	—	—
Allentown-Bethlehem-Easton, Pa.-N.J	—	—	—	—	—	45	56
Philadelphia, Pa	93	82	58	53	—	37	49
Pittsburgh, Pa	—	—	—	—	—	—	—
Wilmington, Del.-N.J.-Md	—	—	—	—	—	—	—
Washington, D.C.-Md.-Va	94	83	—	—	—	27	—
Jacksonville, Fla	92	81	—	—	—	37	—
Miami, Fla	103	92	—	—	—	37	—
Atlanta, Ga	90	80	—	—	—	—	—
Baltimore, Md	93	82	56	50	—	37	—
Norfolk-Portsmouth, Va	94	83	54	46	—	37	—
Charleston, W. Va	—	—	—	—	—	—	58
Huntington, W. Va.-Ashland, Ky	—	—	—	—	—	—	51
Chicago, Ill	86	72	—	59	63	49	53
Gary-E. Chicago-Hammond, Ind	—	—	—	—	—	—	—
Indianapolis, Ind	85	76	—	—	—	—	—
Detroit, Mich	85	77	—	58	60	53	55
Flint, Mich	—	—	—	—	—	—	—
Akron, Ohio	101	90	—	—	—	—	—
Cincinnati, Ohio-Ky.-Ind	—	—	—	—	—	—	—
Cleveland, Ohio	101	90	—	—	—	—	—
Steubenville-Wierton, Ohio-W. Va	—	—	—	—	—	—	54
Toledo, Ohio-Mich	101	90	—	61	—	56	—
Milwaukee, Wisc	88	80	—	—	—	—	—
Birmingham, Ala	90	80	—	—	—	—	—
Louisville, Ky.-Ind	—	—	—	—	—	—	—
Chattanooga, Tenn.-Ga	87	76	—	—	—	—	—
Memphis, Tenn.-Ark	—	72	—	40	—	37	—
Davenport-Rock Island-Moline, Iowa-Ill	—	—	—	—	—	—	—
Kansas City, Mo.-Kan	87	76	—	—	—	34	—
Minneapolis-St. Paul, Minn	89	80	—	63	—	56	—
St. Louis, Mo.-Ill	85	74	—	—	—	44	45
Omaha, Nebr.-Iowa	87	78	—	—	—	—	—
New Orleans, La	88	77	—	45	—	37	—
Oklahoma City, Okla	84	73	—	—	—	34	—
El Paso, Texas	—	—	—	—	—	—	—
Houston, Texas	—	—	—	—	—	34	—
Phoenix, Ariz	—	—	—	—	—	—	—
Denver, Colo	—	—	—	—	—	—	—
Salt Lake City, Utah	—	—	—	—	—	42	—
Los Angeles-Long Beach, Calif	75	67	—	38	—	27	—
San Francisco-Oakland, Calif	—	—	—	—	—	—	—
Portland, Ore.-Wash	—	—	—	53	—	45	—
Seattle-Everett, Wash	—	—	—	54	—	45	—
Honolulu, Hawaii	—	—	—	—	—	44	—

[a] Dash (—) indicates data on oil prices not available.

Table 4–15. INDUSTRIAL CONSUMER PRICES OF NATURAL GAS—1967 [a]

[cents/10⁶ Btu]

Standard Metropolitan Statistical Area	Natural gas	
	Continuous [b]	Interruptible [c]
Hartford, Conn.	143	54
Boston, Mass.	175	36
Providence-Pawtucket	114	—
Buffalo, N.Y.	97	—
New York, N.Y.	130	44
Syracuse, N.Y.	102	68
Allentown, Pa.	88	48
Philadelphia, Pa.	100	33
Pittsburgh, Pa.	52	—
Wilmington, Del.	76	37
Washington, D. C.	90	60
Jacksonville, Fla.	90	40
Miami, Fla.	103	41
Atlanta, Ga.	60	30
Baltimore, Md.	83	50
Norfolk, Va.	79	45
Charleston, W. Va.	65	42
Huntington, W. Va.	65	43
Chicago, Ill.	56	28
Gary, Ind.	43	29
Indianapolis, Ind.	60	40
Detroit, Mich.	55	43
Flint, Mich.	57	41
Akron, Ohio	54	—
Cincinnati, Ohio	55	42
Cleveland, Ohio	54	—
Steubenville, Ohio	49	—
Toledo, Ohio	55	—
Milwaukee, Wisc.	87	49
Birmingham, Ala.	35	31
Louisville, Ky.	60	46
Chattanooga, Tenn.	64	37
Memphis, Tenn.	33	23
Davenport, Ill.	54	26
Kansas City, Kans.	—	24
Minneapolis, Minn.	75	37
St. Louis, Mo.	55	33
Omaha, Nebr.	48	28
New Orleans, La.	23	—
Oklahoma City, Okla.	18	15
El Paso, Texas	44	—
Houston, Texas	25	—
Phoenix, Ariz.	45	—
Denver, Colo.	—	24
Salt Lake City, Utah	37	26
Los Angeles, Calif.	54	32
San Francisco, Calif.	55	38
Portland, Ore.	62	36
Seattle, Wash.	100	35
Honolulu, Hawaii	210	—

another fuel. These costs include replacement of burners, fuel handling changes, and combustion chamber changes. Capital charges in the following example were assumed to be 8 percent per year with straightline depreciation over a 25-year period. A longer depreciation period would, of course, decrease the annual charges. Any credits associated with scrapping of storage and handling equipment for the discontinued fuel are not included in these evaluations, but could at times be valuable. Annualized costs are calculated and determined on an equivalent energy input basis. These annualized costs include capital charges, operation, maintenance, and fuel costs.

The following procedure may be used to determine fuel substitution costs in a specific area:

1. Select a source of sulfur dioxide emission, an industrial boiler of given output rating in pounds steam per hour. (Example: a boiler with a capacity of 100,000 pounds of steam per hour, burning 3.3-percent sulfur coal).
2. Select the possible fuel alternatives and from given boiler efficiencies determine energy input requirements in Btu per hour. (1000 pounds of steam requires approximately one million Btu of heat output).
3. Obtain fuel costs (by sulfur content) for the area of interest. Compute the required fuel cost per year. A sample analysis for Chicago, Ill., is shown in Table 4–17. Fuel costs and sulfur contents are taken from Tables 4–13, 4–14, and 4–15.
4. For the corresponding fuel alternatives, determine the capital investments for boiler modifications and

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[a] Prices are estimated from one of the following: A.G.A. Rate Service, Vols. I and II. American Gas Association, Inc., New York, March, 1968.

Brown's Directory of North American Gas Companies, 81st edition, Moore Publishing Co., Duluth, Minnesota, 1967.

[b] A guaranteed supply 100 percent of the time. Prices represent an estimated rate based on a decending scale rate for higher volume usage.

[c] Gas supplied during times of off-peak demand. Prices and schedules of supply are sometimes negotiated: at other times the rates are already established. Practice is dependent on the local gas utility.

Table 4-16. SULFUR CONTENTS AND PRICES OF COALS IN 1966 BY PRODUCTING DISTRICTS[14, 62-64]

District No. and Name	Sulfur (dry basis), weight percent			Average coal price per ton
	Low	Average	High	F.O.B. mine, dollars
1. Eastern Pennsylvania	1.0	1.8	3.6	4.33
2. Western Pennsylvania	1.1	1.8	4.1	5.97
3. & 6. West Virginia	0.6	2.4	3.8	4.65 & 4.28
4. Ohio	1.6	3.5	5.0	3.79
5. Michigan	—	—	—	—
7. Southern No. 1 (South W. Va. and Western Va.)	0.5	0.7	1.1	6.14
8. Southern No. 2 (Eastern Kentucky)	0.5	1.1	4.3	4.44
9. Western Kentucky	2.0	2.9	4.0	3.45
10. Illinois	1.1	2.7	4.1	3.85
11. Indiana	1.1	3.3	5.3	3.92
12. Iowa	4.2	4.7	5.7	3.69
13. Southeastern (Alabama)	0.7	1.1	1.7	6.76
14. Arkansas-Oklahoma	NA	NA	NA	7.30
15. Southwestern (Mo., Kansas, Texas)	3.0	3.9	6.0	4.29
16. Northern Colorado	0.3	0.5	0.7	4.20
17. Southern Colorado	0.5	0.7	0.9	5.35
18. New Mexico (also Arizona, Calif.)	NA	1.0	NA	2.52
19. Wyoming	0.6	0.9	1.0	3.23
20. Utah	0.6	0.7	0.8	5.77
21. North-South Dakota	0.7	0.8	1.0	1.98[a]
22. Montana	0.6	0.7	0.7	3.08
23. Washington (also Oregon)	NA	NA	NA	7.57

[a] Lignite, 7,000 Btu/lb as received.

NA = not available.

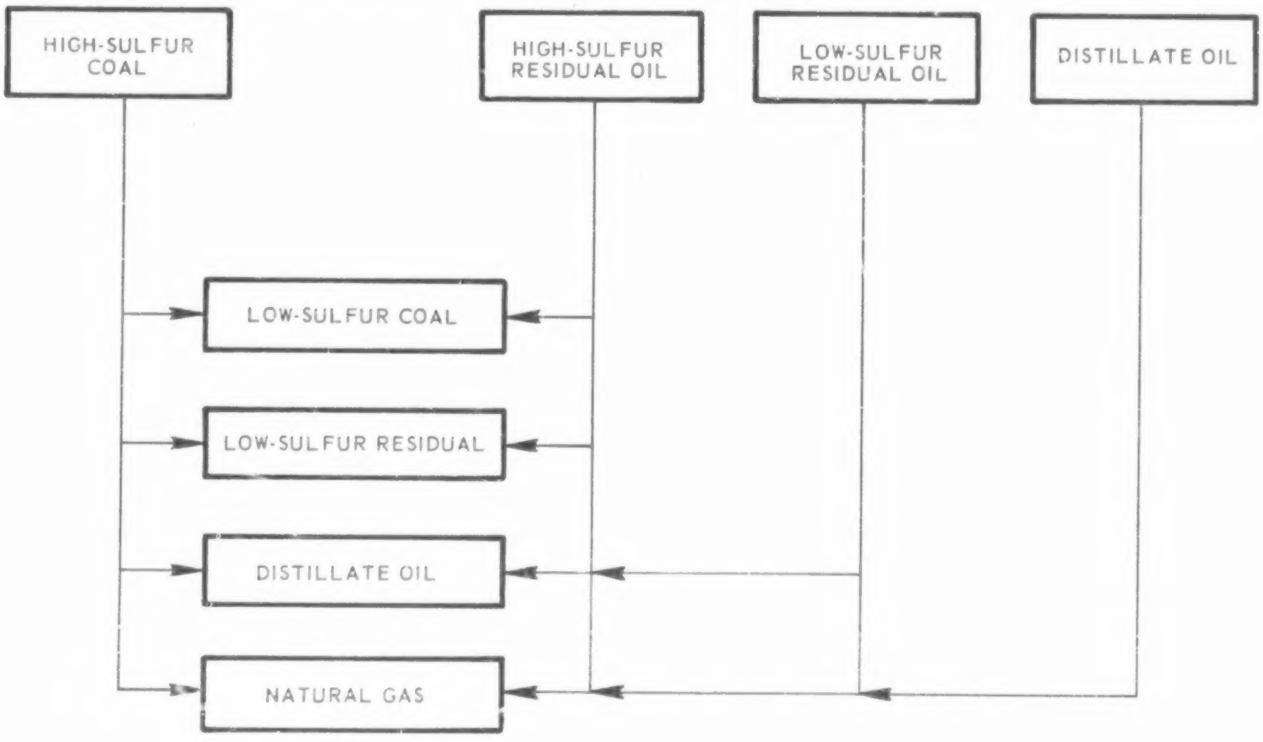
HIGH-SULFUR COAL
HIGH-SULFUR RESIDUAL OIL
LOW-SULFUR RESIDUAL OIL
DISTILLATE OIL
LOW-SULFUR COAL
LOW-SULFUR RESIDUAL
DISTILLATE OIL
NATURAL GAS

Figure 4-12. Fuel substitution schemes for reduction of sulfur oxide emissions.

operation costs. The boiler modification cost may be obtained from the manufacturers or from local fuel supplier.

5. Annualize fuel costs, capital charges, and operating and maintenance costs.
6. For the fuels selected, determine the potential SO_2 emissions for the required equal energy output from the heat and sulfur content of the fuels.
7. Using the original fuel (3.3-percent-sulfur coal) as a baseline for evaluating effectiveness, calculate the emissions for alternative fuels as illustrated in Table 4–18.

In this example, an SO_2 reduction using one alternative, a switch to interruptible gas service was accomplished for very little additional cost. Costs will vary widely from area to area, and from one combustion unit to another.

4.3.3 Fuel Conversion Problems

The National Petroleum Council conducted a study of the extent to which equipment designed to burn various types of fossil fuels could be converted from one type of fuel to another.[65] The Council limited the scope of the study to physical facilities only, without regard to economics or the availability of alternate sources of fuel. Tables 4–19, 4–20, and 4–21 show the convertibility of domestic, commercial, and industrial heating equipment.

The substitution of one type of fuel for another can be an expensive step if the fuel burning equipment cannot be easily converted. In some cases, furnaces are designed to burn solid, liquid, or gaseous fuels; however, most are designed for only one type. Changing from high-sulfur to low-sulfur coal may present problems with ash fusion in wet-bottom furnaces, and may affect the fly ash collection efficiency of electrostatic precipitators.

Changing from a solid to a liquid fuel requires entirely different storage and handling equipment; however, changing from a solid or liquid to a gaseous fuel would not present any storage problems since gas is not stored in large quantities. Eliminating the storage problems by switching to a gaseous fuel would actually reduce overall fuel handling costs. Additional cost benefits may also be realized when factors such as ash handling and elimination of fly ash collectors are taken into account.

Table 4–17. COST AND ENGINEERING DATA FOR TYPICAL FUEL SUBSTITUTION PROBLEM ANALYSIS

[Based on 7000 operating hours per year for 100,000-lb/hr steam boiler]

Fuel	Cost $/$10^6$ Btu	Boiler efficiency, percent	Steam output, 1,000 lb/hr	Energy input, 10^6 Btu/hr	Fuel costs per year, $1,000	Annual charges for boiler conversion, operation, maintenance, $1,000	Total annual costs, $1,000
Coal:							
3.3 percent sulfur	0.31 [a]	87	100	115	250	—	250
1.0 percent sulfur	0.38	87	100	115	306	—	306
No. 6 oil:							
No S. Guar	0.49 [b]	86	100	116	399	4	403
1 percent S. Guar	0.53	86	100	116	431	4	435
No. 5 oil: No S. Guar	0.59	86	100	116	480	4	484
No. 2 oil	0.72	86	100	116	586	4	590
Natural gas:							
Interruptible [d]	0.28 [c]	82	100	122	273	3	276
Firm	0.56	82	100	122	478	3	481

[a] Coal prices for Chicago, Ill., from Table 4–13.

[b] Oil prices for Chicago from Table 4–14.

[c] Gas prices for Chicago from Table 4–15.

[d] Assume 90 percent gas (during off-peak demand) and 10 percent distillate (No. 2) oil.

Table 4-18. EMISSION CONTROL-COST EFFECTIVENESS RATIO OF FUEL ALTERNATIVES

Fuel	Fuel content, Btu/lb	Input, 10^6 Btu/hr	SO_2, lb/hr	Emission,[d] ton/yr	SO_2 reduction, percent	Total annual cost,[c] $1,000/yr	Pollution control cost, $1,000/yr	SO_2 reduction, tons/yr	Cost/ton of SO_2 eliminated, dollars
Coal:									
3.3 percent sulfur	12,000 [e]	115	632	2212	—	250	—	—	—
1.0 percent sulfur	14,000 [e]	115	164	574	74	306	56	1638	34
No. 6 oil:									
No sulfur guar. approx. 2.2 percent [a]	18,800	116	271	949	57	403	153	1263	121
1.0 percent S guar	18,800	116	123	431	81	435	185	1781	104
No. 5 oil, no S guar. approx. 2.0 percent [a]	19,000	116	244	854	61	484	234	1358	173
No. 2 oil, 0.2 percent S approx	19,400	116	36	126	94	590	340	2086	163
Interruptible [b] gas, 0.0005 percent sulfur	21,000	122	4	12	99.5	276	26	2200	12
Firm gas, 0.0005 percent sulfur	21,000	122	—	—	100	481	321	2212	105

[a] An estimated average based on a survey of industrial fuel oil dealers in the Chicago area.

[b] Usage of gas for 90 percent of energy required and No. 2 oil for remaining 10 percent. SO_2 emissions due to No. 2 oil used 10 percent of time.

[c] Costs taken from Table 4-17.

[d] Based on 7000 operating hours.

[e] Heat content does not necessarily depend on sulfur content.

4.4 FUEL DESULFURIZATION

4.4.1 Introduction

Fuel desulfurization, whether partial or complete, offers another way of reducing SO_2 emissions. The economic and technical feasibility of fuel desulfurization, however, varies widely, but this aspect of SO_2 control should always be examined before developing an SO_2 control program for a specific area.

Desulfurization of fuels is not new. Research into ways of removing sulfur from coal, oil, and gas has been going on for many years, and actual commercial desulfurization operations exist. These installations, however, operate only to increase profit or

Table 4–19. CONVERTIBILITY OF INDUSTRIAL HEATING EQUIPMENT

Type of equipment	Designed to burn			Can be converted to burn		
	Coal	Oil	Gas	Coal	Oil	Gas
Incinerators		X[a]		No	NA[b]	Yes
			X	No	Yes	NA
Boilers	X	X		NA	NA	Yes
	X		X	NA	Yes	NA
		X	X	No	NA	NA
	X			NA	Yes	Yes
		X		Perhaps	NA	Yes
			X	Perhaps	Yes	NA
Process heating	X	X		NA	NA	Yes
	X		X	NA	Yes	NA
		X	X	No	NA	NA
			X	Perhaps	Yes	NA
Heat treating		X	X	No	NA	NA
		X		No	NA	Yes
			X	No	Yes	NA

[a] Designates the fuel that the equipment was designed to burn.
[b] Not applicable.

Table 4–20. CONVERTIBILITY OF COMMERCIAL HEATING EQUIPMENT

Type of equipment	Designed to burn			Can be converted to burn		
	Coal	Oil	Gas	Coal	Oil	Gas
Unit heaters		X[a]		No	NA[b]	Yes
			X	No	No	NA
Incinerators		X		No	NA	Yes
			X	No	Yes	NA
Portable unvented heaters (salamanders)	X			NA	No	No
		X		No	NA	No
			X	No	No	NA
Water heaters	X			NA	Yes	Yes
		X		No	NA	Yes
			X	No	Perhaps	NA
Warm-air furnaces	X			NA	Yes	Yes
		X		No	NA	Yes
			X	No	Perhaps	NA
Boilers—steam or hot water	X			NA	Yes	Yes
		X		No	NA	Yes
			X	No	Perhaps	NA
		X	X	No	NA	NA

[a] Designates the fuel that the equipment was designed to burn.
[b] Not applicable.

marketability of the fuel. For example, some pyrite sulfur is removed in normal coal preparation operations that are performed to remove clay, shale, and rocks from the coal, and pyrite has been reduced in metallurgical-grade coals for many years. Research efforts to transform coal into liquids and gases involve removal of sulfur, but their primary purpose is the upgrading of coal to more valuable products. In refining crude oils, hydrogen treatment is widely practiced on the distillate oils to meet certain sulfur specifications. Natural gas containing sulfur compounds is desulfurized to increase its marketability and meet specifications.

The impetus given this work by the concern over air pollution is a new aspect. In effect, air pollution regulations that set stringent sulfur levels have created a new market, which has led to greatly increased efforts to develop low-sulfur fuels.

Sulfur can be partially removed from coal by means of coal preparation techniques now available. Much coal is currently being cleaned, to improve its marketability; however, relatively few coals are cleaned extensively. Capability for sulfur reduction varies widely according to the specific coal type.

Liquefaction and gasification of coal may be practiced on a limited scale in 5 to 10 years. However, even then, because of economic considerations, these methods will account for only a small portion of coal used.

Processes for producing residual fuel oil with a sulfur content of 1.0 percent or less are in operation, and numerous additional installations employing processes of this type are in the construction or planning stage.

4.4.2 Coal

4.4.2.1 Introduction—Sulfur exists in coal in three forms; pyrites (FeS_2), organic compounds, and sulfates. The total sulfur content of coal ranges from negligible amounts to about 7 percent by weight.

Sulfates, usually present only in very small quantities, are not considered a problem. Organic sulfur is bound molecularly into coal and cannot be removed without chemically changing the nature of the fuel by liquefaction or gasification. Pyritic sulfur present as particles is removable by physical techniques except when intimately mixed in the coal. The degree of sulfur removal depends on the types of sulfur present in the coal and on the amount of each type present.

This discussion considers only bituminous coal because anthracite coal, which is inher-

Table 4-21. CONVERTIBILITY OF DOMESTIC HEATING EQUIPMENT

Type of equipment	Designed to burn			Can be converted to burn		
	Coal	Oil	Gas	Coal	Oil	Gas
Incinerators		X [a]		No	NA [b]	Yes
			X	No	Perhaps	NA
Unvented space heaters		X		No	NA	No
			X	No	No	NA
Vented space heaters	X			NA	Difficult	Difficult
		X		No	NA	No
			X	No	No	NA
Recessed wall heaters		X		No	NA	Perhaps
			X	No	No	NA
Water heaters	X			NA	Probably	Probably
		X		No	NA	Perhaps
			X	No	No	NA
Warm-air furnaces	X			NA	Yes	Yes
		X		No	NA	Yes
			X	No	No	NA
Boilers—steam or hot water	X			NA	Yes	Yes
		X		No	NA	Yes
			X	No	Perhaps	NA

[a] Designates the fuel that the equipment was designed to burn.

[b] Not applicable.

ently low in sulfur (0.7 percent average), makes up less than 4 percent of coal consumed annually and is steadily decreasing in use.

4.4.2.2 Pyrite Removal: Coal Preparation—Coal preparation or cleaning is the mechanical removal of impurities from coal. The extent and type of cleaning depend on the nature of the coal and on its projected use. Coal for steam generation must meet specifications different from those for coal for metallurgical coke production.

Mechanical cleaning of coal is possible because of the differences in physical properties between coal and its impurities. Specific gravity is the property most often exploited, normally by a water-washing process. Table 4–22 lists the chief cleaning methods utilized in the coal industry.[66]

A typical coal preparation operation is diagrammed in Figure 4–13.

Selective mining is the first step in production of coal of a consistent desired quality. Mechanically mined coal contains considerably more rock, shale, and fine coal particles than manually mined coal, and may require additional cleaning. This cleaning usually lowers the sulfur content by removing the larger particles of heavy pyrite. The Brookdale, Pa., plant of the Bethlehem Steel Corporation for some time has been reducing sulfur content of coal from 3.4 percent to 1.0 percent at a total product yield of 85 percent. An existing, fairly sophisticated, 500-ton-per-hour coal-preparation plant is diagrammed in Figure 4–14 in order to show the complexity of such an operation. Costs of this operation are detailed in Table 4–23.

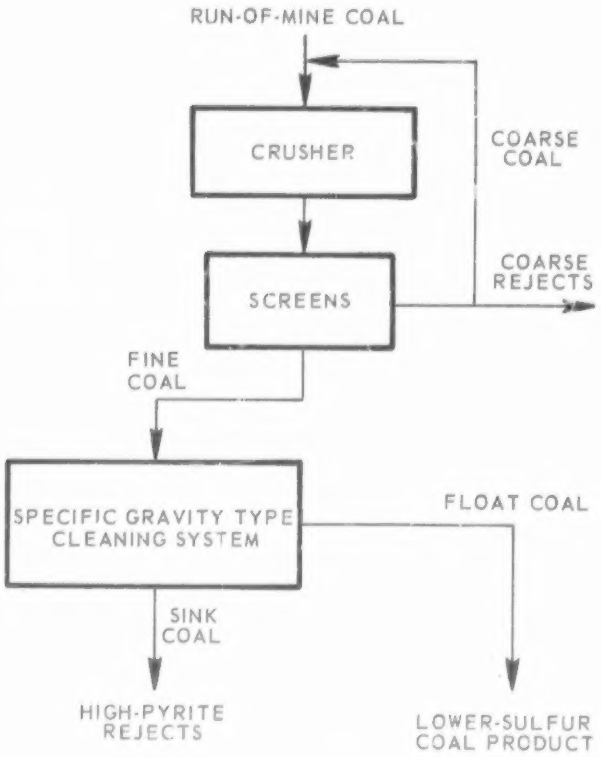

Figure 4-13. Coal preparation (simplified flow chart).

In 1964, the Paul Weir Company reported on a study entitled "The Economic Feasibility of Coal Desulfurization." Sulfur reduction data from that study are summarized in Table 4–24. Total sulfur, organic sulfur, and cleaned-coal sulfur percentages vary widely within the individual States and coal beds. Because of a lack of data on type and levels of sulfur in coal beds, on the washability of the pyritic sulfur, and on capability of available cleaning methods for pyrite separation, the study did not produce definitive results. In 1965, the Public Health Service funded a study by the Bureau of Mines to determine the washability of pyritic sulfur in the major sources of fuel coals. In 1966, to accelerate this study, a contract was let to Commercial Testing and Engineering Company to determine washability of pyritic sulfur in selected areas believed to have washable coals. In this same year, a study was funded with the Illinois Geological Survey to determine the important chemical and physical properties of all coal beds actively mined in Illinois.

Figure 4–15 shows organic, pyritic, and total sulfur levels of coal based on the cumulative data obtained in these studies to date. The small sulfate fraction of the sulfur is included in the organic portion. This figure shows the technical feasibility of reducing pyrite sulfur by presently employed washing (float and sink) techniques. The upper portion of the pyrite sulfur in Figure 4–15 may be removed if the coal is crushed to $\frac{3}{8}$ inch and floated in a liquid of specific gravity 1.60, but the lower portion of the pyrite is too intimately mixed to be removed by this treatment. Of the mines sampled, about 20 percent

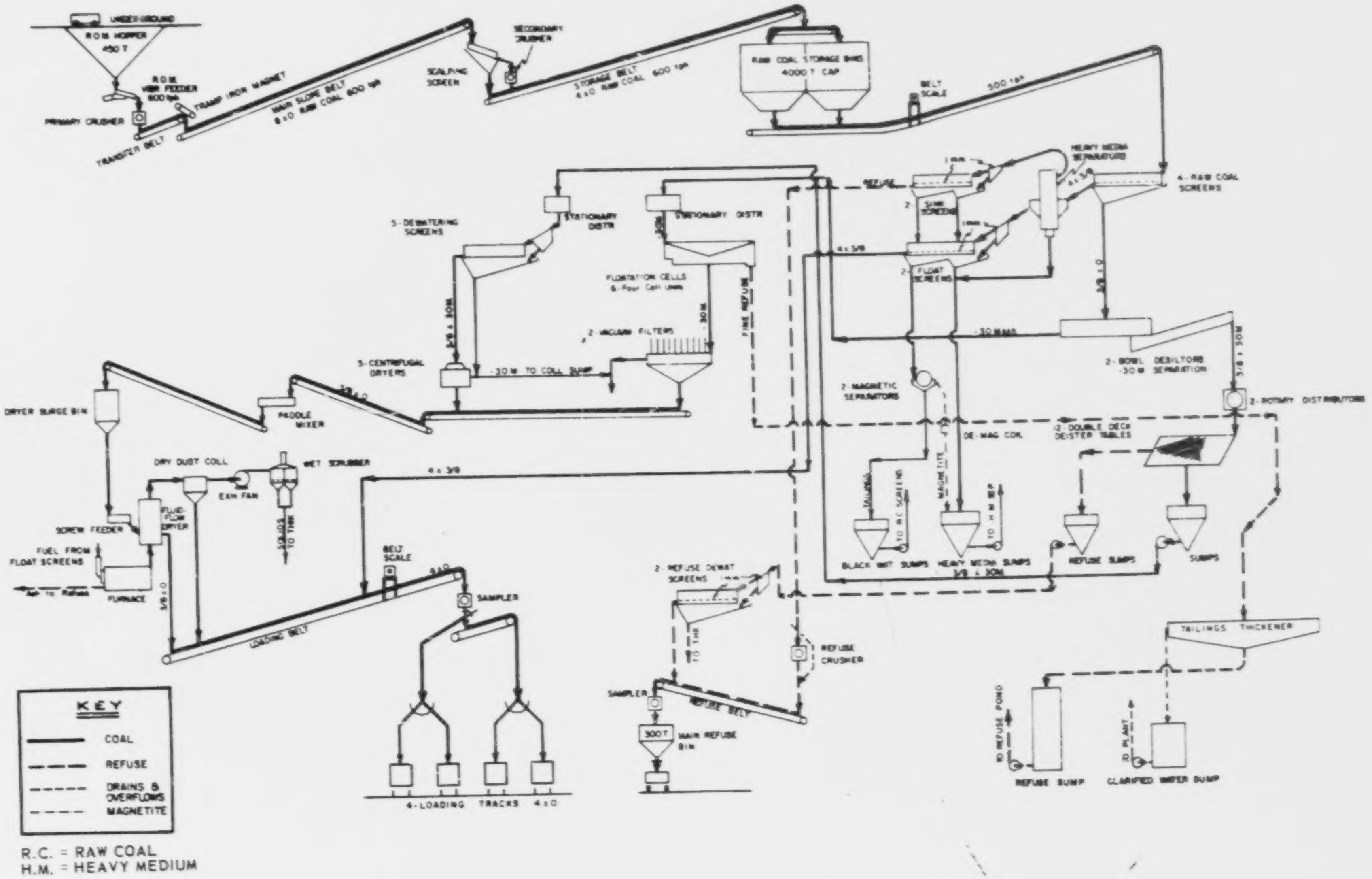
UNDERGROUND
ROM HOPPER
450 T
ROM
VIBR FEEDER
800 tph
PRIMARY CRUSHER
TRANSFER BELT
TRAMP IRON MAGNET
MAIN SLOPE BELT
8 x 0 RAW COAL 800 tph
SCALPING SCREEN
SECONDARY CRUSHER
STORAGE BELT
4 x 0 RAW COAL 600 tph
RAW COAL STORAGE BINS
4000 T CAP
BELT SCALE
500 tph
HEAVY MEDIA SEPARATORS
4 x 3/8
4 - RAW COAL SCREENS
1mm
REFUSE
2 - SINK SCREENS
2 - FLOAT SCREENS
4 x 3/8
3/8 x 0
-30 Mesh
2 - BOWL DESILTORS
-30 M SEPARATION
3/8 x 30 M
2 - ROTARY DISTRIBUTORS
12 - DOUBLE DECK DEISTER TABLES
DE-MAG COL
2 - MAGNETIC SEPARATORS
TAILINGS
TO R.C. SCREENS
MAGNETITE
TO H.M. SEP
BLACK WAT SUMPS
HEAVY MEDIA SUMPS
3/8 x 30M
REFUSE SUMPS
SUMPS
TAILINGS THICKENER
TO REFUSE POND
REFUSE SUMP
TO PLANT
CLARIFIED WATER SUMP
STATIONARY DISTR
STATIONARY DISTR
30M
5 - DEWATERING SCREENS
FLOTATION CELLS
6 - Four Cell Units
FINE REFUSE
3/8 x 30M
-30M
2 - VACUUM FILTERS
5 - CENTRIFUGAL DRYERS
-30 M TO COLL SUMP
3/8 x 0
PADDLE MIXER
DRYER SURGE BIN
DRY DUST COLL
WET SCRUBBER
EXH FAN
SOLIDS TO THKR
FLUID-FLOW DRYER
SCREW FEEDER
FUEL FROM FLOAT SCREENS
Ash to Refuse
FURNACE
3/8 x 0
4 x 3/8
BELT SCALE
4 x 0
SAMPLER
LOADING BELT
4 - LOADING TRACKS 4 x 0
2 - REFUSE DEWAT SCREENS
1mm
TO THK
REFUSE CRUSHER
SAMPLER
REFUSE BELT
300 T
MAIN REFUSE BIN
KEY
COAL
REFUSE
DRAINS & OVERFLOWS
MAGNETITE
R.C. = RAW COAL
H.M. = HEAVY MEDIUM

Figure 4-14. Flowsheet of a 500 ton/hr coal preparation plant.[71]

Table 4-22. EXISTING MECHANICAL METHODS OF CLEANING COAL

Physical property	Method	Size treated	Percent of cleaned coal utilizing method
Crushability and size	Crushing and screening	6 in. and up	Initial step in most cleaning operations
Specific gravity	Jig	6 mesh—3 in	47.8
	Heavy medium	6 mesh—8 in	27.2
	Table	100 mesh—1/4 in	13.2
	Pneumatic	Up to 1/4 in	6.9
	Cyclone	1/8 in—1 1/2 in	2.2
	Launder	4 mesh—3 in	1.9
Surface effect	Froth flotation	Up to 30 mesh	—

produced coal that was washable to 1 percent sulfur or less, and 45 percent produced coal that was washable to 2 percent sulfur or less by crushing to 3/8 inch and floating in a liquid of specific gravity 1.60. These percentages represent a total of about 13.5 million and 29.6 million tons of coal annually.

The economic aspects of coal cleaning, by the best available techniques, were explored by the Paul Weir Company under its 1964 contract. Cost data were computed on the basis of a hypothetical 1000-ton-per-hour plant. This proposed plant, diagrammed in Figure 4–16, reduces the coal to a final maximum size of 3/8 inch. The dried product is about 78 percent of the input mine coal; the other 22 percent, rejected at various process points, is considered nonrecoverable. Estimated costs per ton for products of this plant are shown in Table 4–25. Sulfur contents are not given since this would depend on the specific type of coal.

The economic feasibility study points out many knowledge gaps, such as insufficient data on sulfur distribution and characteristics in a given coal seam, the washability of a given coal seam, and the capabilities of present cleaning operations.

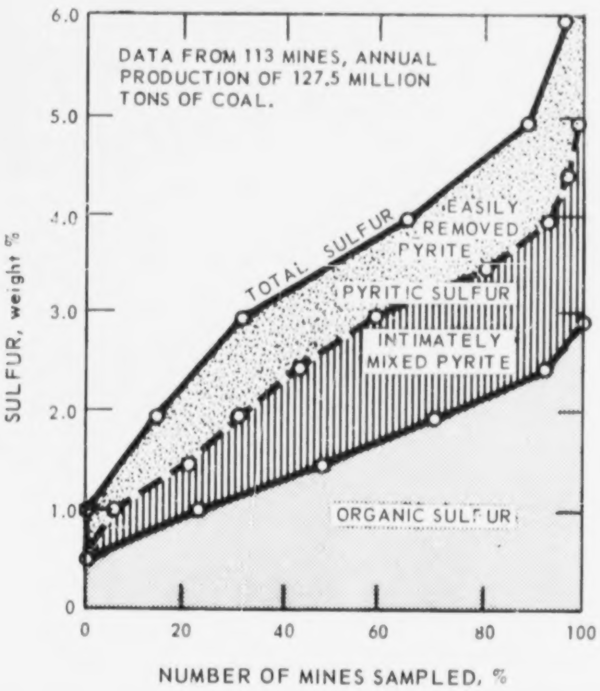

Figure 4-15. Maximum sulfur content versus percent of mines sampled.[68]

Table 4-23. COST DATA FOR 500-TON-PER-HOUR COAL PREPARATION OPERATION[67]

Greene County, Pennsylvania—Pittsburgh bed:	
Coal crushed to 1½ in.[a]	
Coal washed by 1.60 specific gravity separating medium	
Costs:	
Mining costs per ton	$3.60
at 90 percent yield	4.00
(10% list in cleaning process)	
Process costs (per ton of product):	
Operating	$0.415
Depreciation (20 year)	0.117
Mining	4.000
Total	$4.532 per ton
Cost per 10^6 Btu (at 13,400 Btu/lb.)	$0.169
Total cleaning cost	$0.932 per ton
Sulfur content, percent:	
Raw coal sulfur, 2.66	
Post-wash sulfur, 2.03	
Organic sulfur, 0.95	

[a] Crushing to 3/8 inch would increase operating costs and decrease yield; however, the post-wash sulfur level would be lower.

Table 4-24. TYPICAL SULFUR REDUCTIONS ACHIEVED IN VARIOUS HIGH-SULFUR COAL BEDS

State	Coal districts	Total S, percent range	Organic S, percent range	S range of float coal at top sizes, percent		
				$1\frac{1}{2}$ in.	$\frac{3}{8}$ in.	14 mesh
Pennsylvania-Maryland	1 and 2	0.50-6.30	0.18-1.77	0.65-2.70	0.58-2.48	0.69-2.04
West Virginia	3 and 6	0.50-5.00	0.30-2.06	0.72-3.90	0.71-3.72	0.72-2.57
Ohio	4	1.50-6.40	0.44-2.89	0.80-4.72	0.68-4.28	1.00-3.67
Kentucky	9	1.10-4.70	0.69-1.12	0.83-3.20	0.72-1.55	0.63-1.61
Tennessee	8	0.50-4.40	0.26-2.00	0.84-2.58	0.90-2.30	1.01-2.22
Illinois	10	1.00-6.50	0.60-3.00	1.02-4.68		
Indiana	11	0.80-7.60	0.60-2.40	0.90-3.72		
Iowa	12	3.00-5.60	1.27-2.15	3.57-4.40		
Alabama	13	0.50-3.00	0.33-1.24	0.69-2.03		
Arkansas-Oklahoma	14	0.70-3.00	0.55-1.10	0.90-2.00		

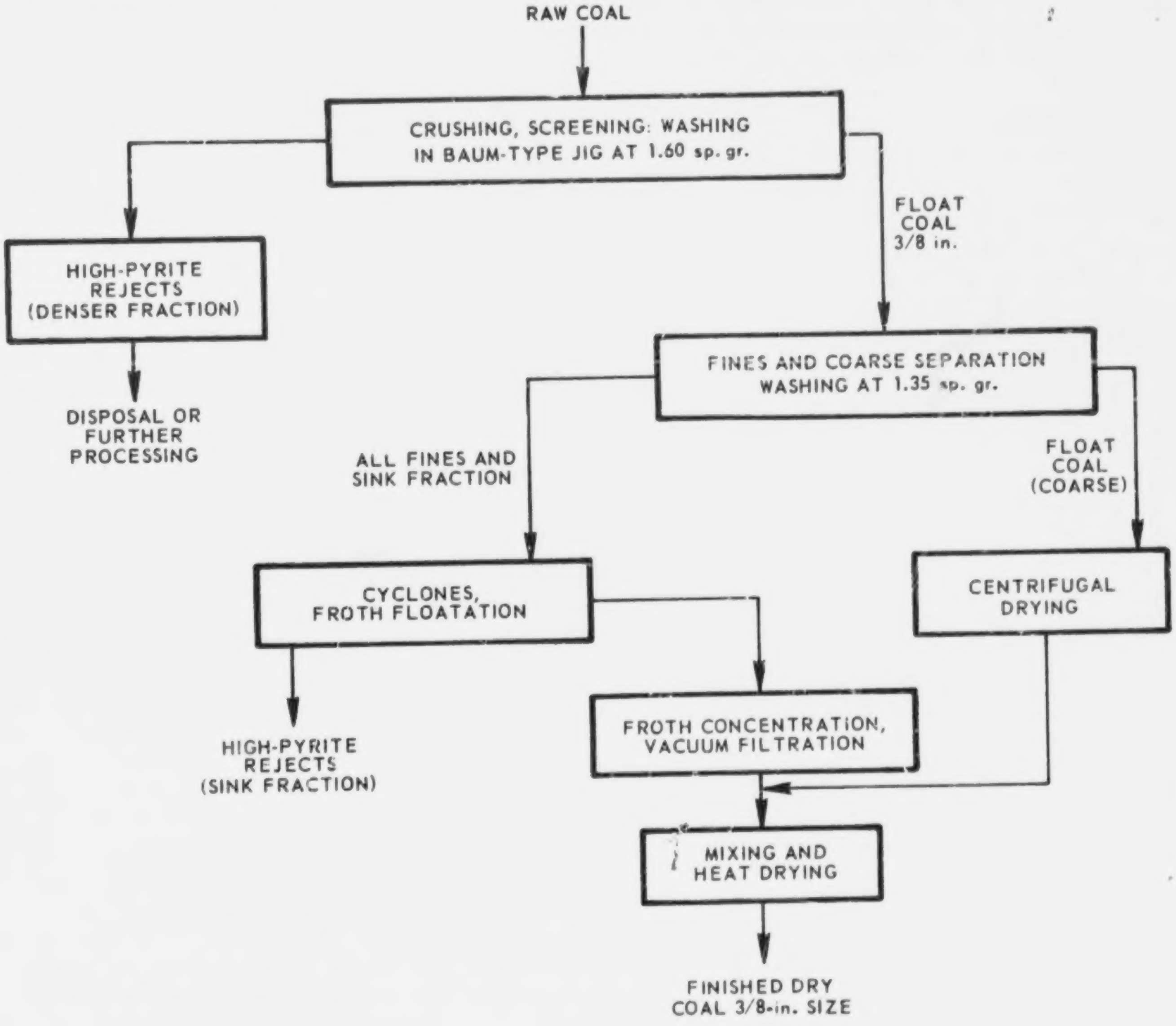
RAW COAL
CRUSHING, SCREENING: WASHING IN BAUM-TYPE JIG AT 1.60 sp. gr.
HIGH-PYRITE REJECTS (DENSER FRACTION)
DISPOSAL OR FURTHER PROCESSING
FLOAT COAL 3/8 in.
FINES AND COARSE SEPARATION WASHING AT 1.35 sp. gr.
ALL FINES AND SINK FRACTION
FLOAT COAL (COARSE)
CYCLONES, FROTH FLOATATION
CENTRIFUGAL DRYING
HIGH-PYRITE REJECTS (SINK FRACTION)
FROTH CONCENTRATION, VACUUM FILTRATION
MIXING AND HEAT DRYING
FINISHED DRY COAL 3/8-in. SIZE

Figure 4-16. Proposed coal cleaning plant[66] (simplified flow chart).

Table 4-25. ESTIMATED PRODUCT COST UTILIZING PROPOSED 1000-TON-PER-HOUR COAL PREPARATION PLANT[67]

	per ton product
Capital costs (20-yr. retirement)	$0.117
Direct operating costs (2,400,000 tons/yr.)[a]	0.370
Coal costs; at 78% yield	3.141
Total	$3.628
Total cost per 10^6 Btu at 12,000 Btu/lb.[b]	$0.151

[a] Do not include taxes.

[b] Final sulfur content will depend on type of raw coal.

The current fuel research program being funded by the Nationl Air Pollution Control Administration is to determine:

1. Efficiency and applicability of available coal cleaning methods for pyrite separation.
2. Available sources of high-sulfur coals capable of being desulfurized.
3. Costs and technical limitations of proven technology for converting the refuse from coal cleaning into useful products.

A logical way to decrease the cost of desulfurization is to find suitable uses for high-pyrite refuse material. Both iron oxides and sulfur can currently be recovered, but the cost of this recovery is too high. At present, fluidized-bed roasting of pyrite and subsequent sulfuric acid manufacture are in the advanced stages of technological development. Design of prototype pyrite-use processes will be initiated early in 1970, depending on performance of the prototype coal-cleaning plant and on the results of pyrite-use studies.

4.4.2.3 Pyrite Removal: Dry Processes—Dry processes for the removal of pyrites from coal are attractive because they can use fine coal and they do not require water. These processes include air classification and electrostatic and magnetic separation, none of which has reached the commercial stage. For each of these processes, coal must be pulverized below 200-mesh size to liberate the finely disseminated pyrite particles for removal. The most advanced of these processes is the two-stage air classification method used by Bituminous Coal Research, Inc. (BCR).

BCR, in cooperation with a group of interested utilities, has installed a pilot plant at the Seward, Pennsylvania, power station of the Pennsylvania Electric Company to study the process. The 3- to 4-ton-per-hour plant will supply pulverized coal to one burner of a boiler. Coarse pyrite will be removed by the tramp iron chute on the pulverizer; 20 to 30 percent of the pyrite can be removed in this manner. Fine pyrite will be removed by an efficient air classifier. Rejects from both the tramp iron chute and the classifier will be further cleaned on a concentrating table. The table will produce clean pyrite, mixed refuse, and clean coal. The clean coal will be returned to the pulverizer, the refuse discarded, and the pyrite sold. Pyrite reduction in the pulverized coal delivered to the consumer is expected to be 60 to 70 percent based on the raw coal. Initially, central Pennsylvania coals, which are low in organic sulfur and high in pyrite, will be used. Losses in the processes are expected to be between 10 and 15 percent since rejects are reprocessed. No by-product credit is assumed.

Magnetic separation of pyrite from coal is being studied at the U.S. Bureau of Mines and at West Virginia University. The work at the Bureau is aimed at enhancing the weak magnetism of pyrite by means of microwave radiation. West Virginia University is examining the use of superconducting magnets to provide higher field intensities for pyrite separation. Both processes are in the basic research stage, as is electrostatic separation of pyrite from coal, which is being studied by the U.S. Bureau of Mines.

4.4.2.4 Liquefaction—Liquefaction is the conversion of coal into products of which the major useful fraction is liquid. Some gaseous products always result, and the major product (up to 50 to 60 percent of yield) is relatively high-sulfur char. Almost all liquefaction processes involve hydrogenation and aim for maximum gasoline production; therefore very little heavy fuel is produced. An exception is the solvent refining (Pemco) process, the end-product of which is a low-ash, low-sulfur liquid or solid fuel.

Liquefaction is not a desulfurization process per se, because the sulfur is not simply removed, but appears in the various end-products. Of major interest in air pollution control is production of a low-sulfur fuel, either as a primary product of the process or by desulfurization of the char.

Coal liquefaction has been a technical reality for decades. The economics of this process in this country, however, have been unfavorable up to now. Coal desulfurization by liquefaction is a possible long-term approach to providing low-sulfur fuels.[69]

Four major liquefaction processes are described in the Appendix 1.

4.4.2.5 Gasification—Gasification is the process in which coal reacts with oxygen, steam, hydrogen, carbon dioxide, or a mixture of these, to produce a gaseous product suitable for pipeline transmission and subsequent use as a fuel. Gasification is an effective method of desulfurization because sulfur is readily removed and recovered as H_2S. Coal gasification is not a new development. Carbonization (pyrolysis) of coal to coke yields a gas that was used as early as 1792 for street lighting in cities throughout the world. This gas is low in heat content because it contains only 15 to 30 percent of the input coal's Btu content. In hydrogasification, the methane is directly produced from coal and contains 57 to 71 percent of the coal's Btu content. The most promising approach is gasification followed by methane shift reaction, which produces a gas having as much as 75 percent of the Btu content of the input coal.

The four major processes for obtaining from coal a gas with heat contents of 900 to 1000 Btu per cubic foot use variations of gasification-methanation. These processes are hydrogasification, CO_2 accepter, molten salt, and two-stage superpressure. Much development is necessary if any of these four processes is to become commercially feasible in the next decade. These methods are also described in the Appendix 1.

The cost of obtaining pipeline-quality gas by these coal gasification techniques is estimated at from \$.44 to \$.54 per 10^6 Btu, which is within the cost range of higher-cost natural gas. The future of gasification appears to lie in providing not a replacement for natural gas, but a supplement, as the cost of finding and using natural gas reserves increases. As a long-range, supplementary source of low-sulfur fuel, this method has promise for the future. Pipeline transmission of gas is generally more economical than transmitting electricity, and the production of this sulfur-free fuel will allow generation of electricity closer to the highly populated areas.

4.4.3 Oil

4.4.3.1 Introduction—All crude oil contains some sulfur. Refining processes—including distillation and cracking, which separate the crude oil into various petroleum products—cause the sulfur to become more concentrated in the heavier fractions, which have higher boiling temperatures. It is the heaviest fraction, petroleum residuum, from which residual fuel oils (primarily Grade 6) are obtained.

Production of residual fuel oil with a sulfur content of 1.0 percent or less is currently receiving much attention. Low-sulfur residual fuel oil can be obtained by direct desulfurization of the high-sulfur residual oil, or indirectly by blending heavy oil fractions with low-sulfur distillate oils. This latter scheme is currently being used to produce most of the imported residual fuel oil with a sulfur content of 1.0 percent or less.

Direct desulfurization by hydrogen treatment of the lighter petroleum products such as distillate fuel oils has been practiced for many years as part of the normal refining process. The application of these methods directly to heavy fuel oils is, however, relatively new. The petroleum industry has further developed and applied these desulfurization schemes successfully as evidenced by some of the new processes being installed, as shown in Table 4–26. A 30,000-barrel-per-day desulfurizing unit has been in operation at Shell Oil Company's refinery at Curacao, Netherlands Antilles, since late 1967. An additional unit costing \$35.5 million is planned by Shell for Punta Cardon, Venezuela. Standard Oil of New Jersey is planning to invest about \$200 million in desulfurizing processes at refineries in western Venezuela and in Aruba, Netherlands Antilles. The installation at Amuay, Venezuela, will consist of three desulfurization units with a total capacity of 159,000 barrels per day of low-sulfur fuel oils.

Many of these schemes upgrade the feed stream to low-sulfur distillate products. These products may be marketed, or blended with heavy oil fractions to yield a fuel oil meeting Grade 6 fuel specifications with a sulfur content of 1.0 percent or less. Under certain operating conditions, however, some of these processes will directly yield a low-sulfur residual fuel oil.

Cost estimates for direct desulfurization of residual fuel oil may be made if the sulfur and metallic content of the crude oil, the cost of hydrogen, the plant size, desired sulfur level, and related factors are known. Costs of reducing sulfur content of residual oil to 1.0 percent range from \$.25 to \$.75 per barrel.[71] Data obtained by the Bechtel Corporation for a typical Caribbean crude oil show an additional cost of \$.60 per barrel (\$.10 per 10^6 Btu) for desulfurizing residual fuel oil from 2.6 to about 1.0 percent, when a 5-year payout was assumed.[72, 73] Another recent cost estimate by Arthur G. McKee and Company was based on domestic crude oils, and showed a breakeven or slightly profitable operation for producing residual fuel oil with a sulfur content of 0.5 percent.[70]

The price of a barrel of residual fuel oil with a sulfur content of 1.0 percent or less, however, cannot be so easily estimated since this price depends on demand, investment payouts, desired profits, import duties, cost of crude oil, value of other refinery products, and quantity purchased.

4.4.3.2 Major Processes for Desulfurization—Several schemes are available for desulfurizing petroleum products. The particular scheme to be used in a given situation will depend on such things as desired sulfur content, type of feed stream and its metals content, and the desired product.

Hydrodesulfurization—Direct residual oil desulfurization processes use a form of hydrocracking for sulfur removal (Section 5.2.-2.3). Hydrocracking processes were originally developed to reduce the yield of residual fuel oil; however, by selecting the proper catalyst and operating conditions, residual fuel oil yields can be maintained and sulfur removal achieved. In deep desulfurization (to

Table 4-26. TYPICAL RECENT PETROLEUM DESULFURIZATION ACTIVITY[70]

Company	Location	Process	Feed
Cities Service	Lake Charles, La.	H-Oil	Residual oil[a]
Idemitsu Kosan	Chiba, Japan	Isomax	Residual oil[a]
Shell	Curacao, N. Ant.	Shell HDS	Vacuum gas oil[a]
Humble	Bayonne, N. J.	Blending[a]	——
Humble	Linden, N. J.	H-Oil	Residual oil
Creole	Amuay, Venezuela	Esso HDS	Vacuum gas oil
Lago	Aruba, N. Ant.	Esso HDS	Vacuum gas oil
Shell	Cardon, Venezuela	Shell HDS	Vacuum gas oil
Aminoil	Kuwait	Isomax	Atmos. residuum
Kuwait National Petroleum	Kuwait	H-Oil	Residuum
Idemitsu Kosan	Japan	Isomax	Residuum
Dikyo Oil	Japan	Gulfining	Vacuum gas oil
Nippon Petroleum	Japan	Isomax	Vacuum gas oil
Toa Nenryo	Japan	Esso Hydrofining[b]	Vacuum gas oil
	Japan	Isomax	Vacuum gas oil
Atlantic Richfield	Wilmington, Calif.	Coker Expansion	——
Phillips Petroleum	Woods Cross, Utah	De-asphalting	Asphalt
Standard of California	El Segundo, Calif.	Coker	——
Texaco	Wilmington, Calif.	Coker[c]	——

[a] Plants in operation; others are under construction or planned.

[b] Two units.

[c] Texaco also is using their partial-oxidation synthesis process to make hydrogen, using residual oil as feed.

below 0.5 percent), however, the yield of residual fuel oil decreases, since the severe operating conditions that must be used tend to upgrade part of the feed to lighter petroleum products.

The three most commercially advanced hydrocracking processes are the H-Oil, ISOMAX, and Gulf-HDS processes. Developed by Hydrocarbon Research, Inc., and Cities Service Oil Company, the H-Oil process has been in commercial operation since late 1962 with a 2500-barrel-per-day installation at Lake Charles, Louisiana, which converts residual oil to lighter products. This process uses an ebullating catalyst system in which the reactor feed (gas and liquid) passes upward through a bed of catalyst maintained in continuous random motion by the upflow. A flow chart for this desulfurization process is shown in Figure 4–17.

The ISOMAX hydrocracking process, developed by Chevron Research Company and Universal Oil Products, Inc., has long been used for distillate-gas oil conversion. Upgrading of low-value residual fractions and desulfurizing of fuel oil are relatively new uses for this process. By controlling the severity of hydrocracking, a heavy, low-sulfur fuel-oil blend stock, as well as minimal yields of synthetic naphtha and saleable gas, are produced. Minimizing the cracking of low-boiling products saves hydrogen and produces a maximum yield of finished fuel oil. Hydrocarbon flows through the reactor once, and hydrogen is recycled from the high-pressure separator. A product stripper is used to remove H_2S. This process is used in a new installation in Chiba, Japan.

The Gulf-HDS process, developed by Gulf Research and Development Company, is also a fixed-catalyst-bed process used to upgrade or desulfurize petroleum residues by catalytic hydrogenation. It produces refined heavy fuel oil and high-quality catalytic-cracker charge stock.

Hydrogen treating—Hydrogen treating is

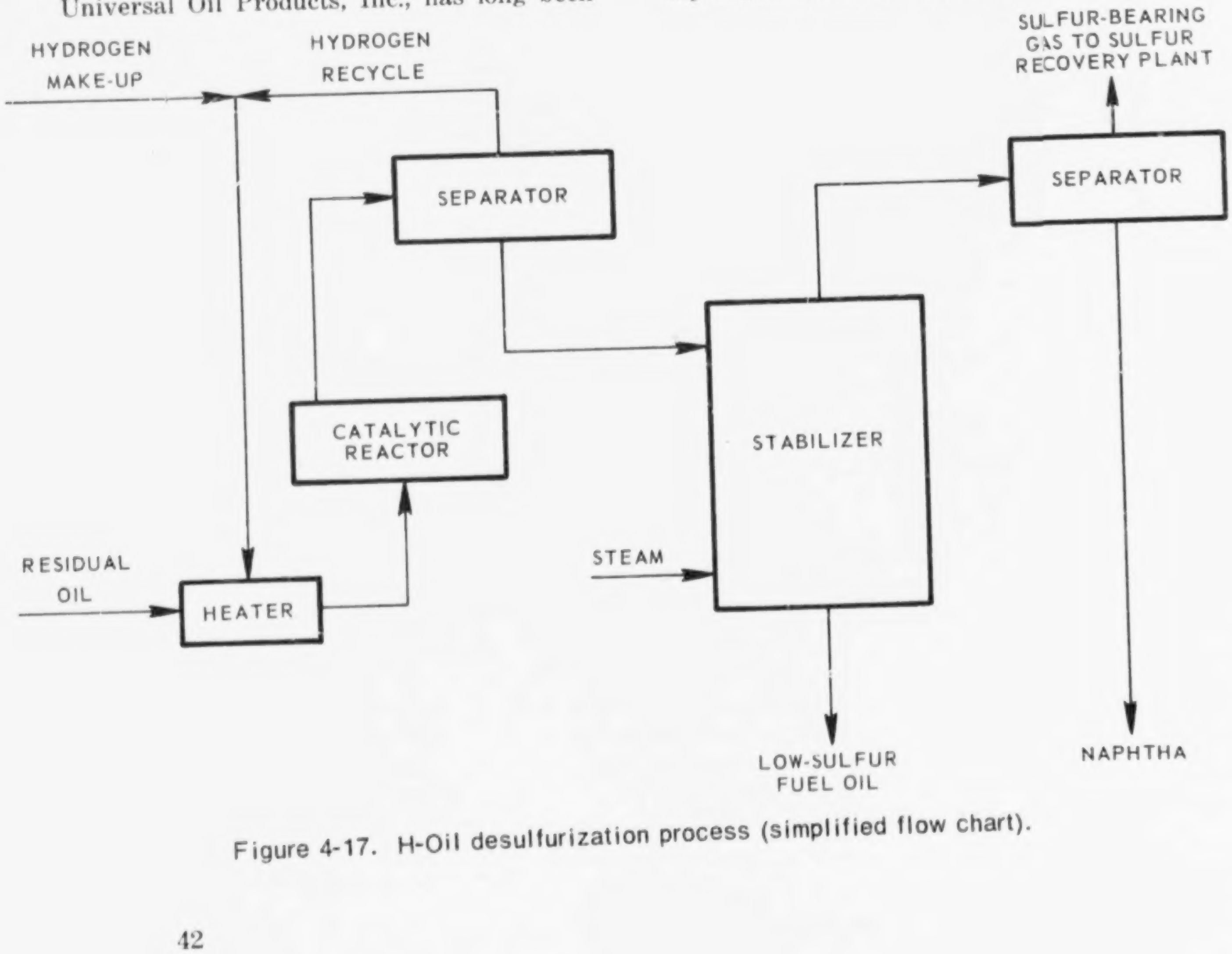

Figure 4-17. H-Oil desulfurization process (simplified flow chart).

an important adjunct to all direct desulfurization operations and is essentially a mild form of hydrocracking. Hydrogen treating is used for hydrogen saturation of olefins and/or aromatics and for removal of sulfur, nitrogen, and other impurities (Section 5.2.2.6). It is widely used in reformer and catalytic cracker feedstock preparation, product upgrading, yield improvement, and sulfur recovery.

The general process flow is shown in Figure 4–18. Feedstock is mixed with hydrogen, heated, and charged to a fixed-bed reactor containing a nickel or cobalt-molybdate-alumina catalyst. The reactor effluent is cooled, separated from recycle gas, and stripped of H_2S and light ends. Operating costs are \$.10 to \$.20 per barrel.[74] Capacity for hydrogen treating in the United States is currently over 3.5 million barrels per day.

Distillation—For a relatively small sulfur reduction (2.6 to 2.0 percent), distillation followed by hydrodesulfurization of the overhead stream may be used. Usually, vacuum distillation is used, but in some cases atmospheric distillation may be satisfactory. The advantage of distillation is that it is relatively inexpensive and makes use of well known technology and existing equipment. Vacuum distillation of the heavy fraction from an atmospheric distillation unit will increase the recovery of the lighter fractions suitable for hydrodesulfurization.

Delayed Coking—Coking is a thermal process for decomposing, rearranging, or combining hydrocarbon molecules by applying heat without catalysts. Delayed coking is a semicontinuous process for the conversion of heavy low-grade oils such as reduced crude and tars into solid coke and lighter products that can be used as catalytic cracking feedstock. This process is important from a fuel desulfurization standpoint since the sulfur is concentrated in the petroleum coke. Disposal of this high-sulfur coke is a problem and may be an economic debit.

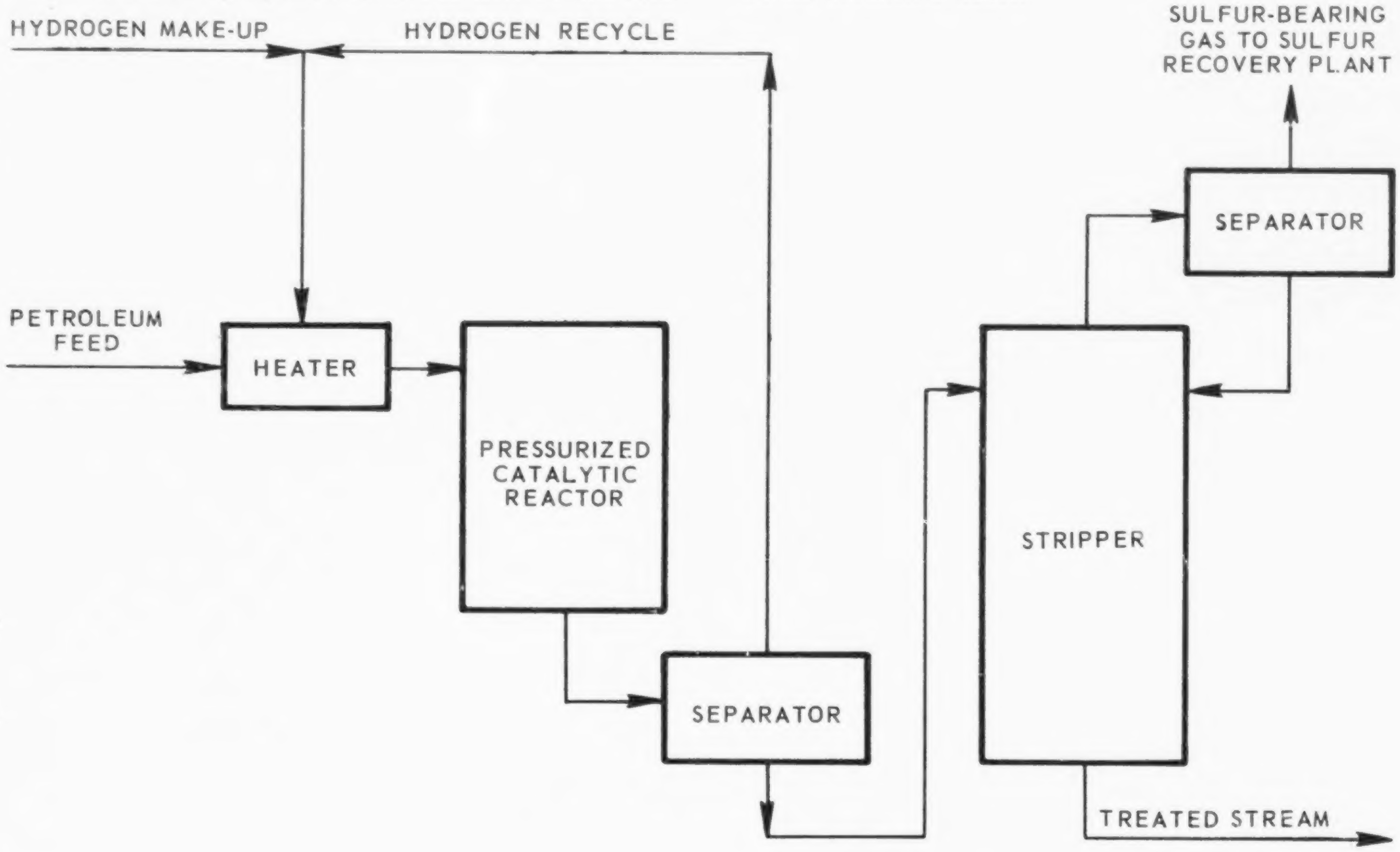

Figure 4-18. Hydrogen treating (simplified flow chart).

Figure 4–19 is a flow chart of the delayed-coking process. Heated charge is introduced into the fractionating tower. Heavy liquids from the tower bottom are pumped through a heater to a coke drum. Vapor from the drum is returned to the fractionating tower for separation into coke gas, gasoline, and gas oil. When a coke drum is full, it is removed from the line and dumped while the process flow is diverted to a clean drum.

In 1964, the capacity of delayed-coking processes in the United States and Canada was about 700,000 barrels per day. For a 15,000-barrel-per-day plant, operating costs in 1962 were estimated at $.30 per barrel.[74]

Solvent De-Asphalting—Solvent de-asphalting is a physical process in which a solvent is used to separate the various constituents of a petroleum charge. In this process, sulfur and heavy metals are removed, color is improved, and carbon residue and the tendency toward coke formation are reduced. Solvent de-asphalting is an alternate method for preparing feedstock for catalytic cracking. It competes with vacuum distillation, coking, and visbreaking.

The process flow is shown in Figure 4–20. The solvent, liquid propane, is contacted counter-currently with descending heavy oil in the de-asphalting (contacting) tower. The normal charge stock is vacuum-reduced crude of various boiling ranges. The de-asphalted oil is separated from propane by evaporation and steam stripping. The heavy asphalt-propane mixture is heated, flashed, and stripped. Propane is recovered and compressed for reuse. Residual fuel oil with a sulfur content of 1 percent or less can be achieved by this

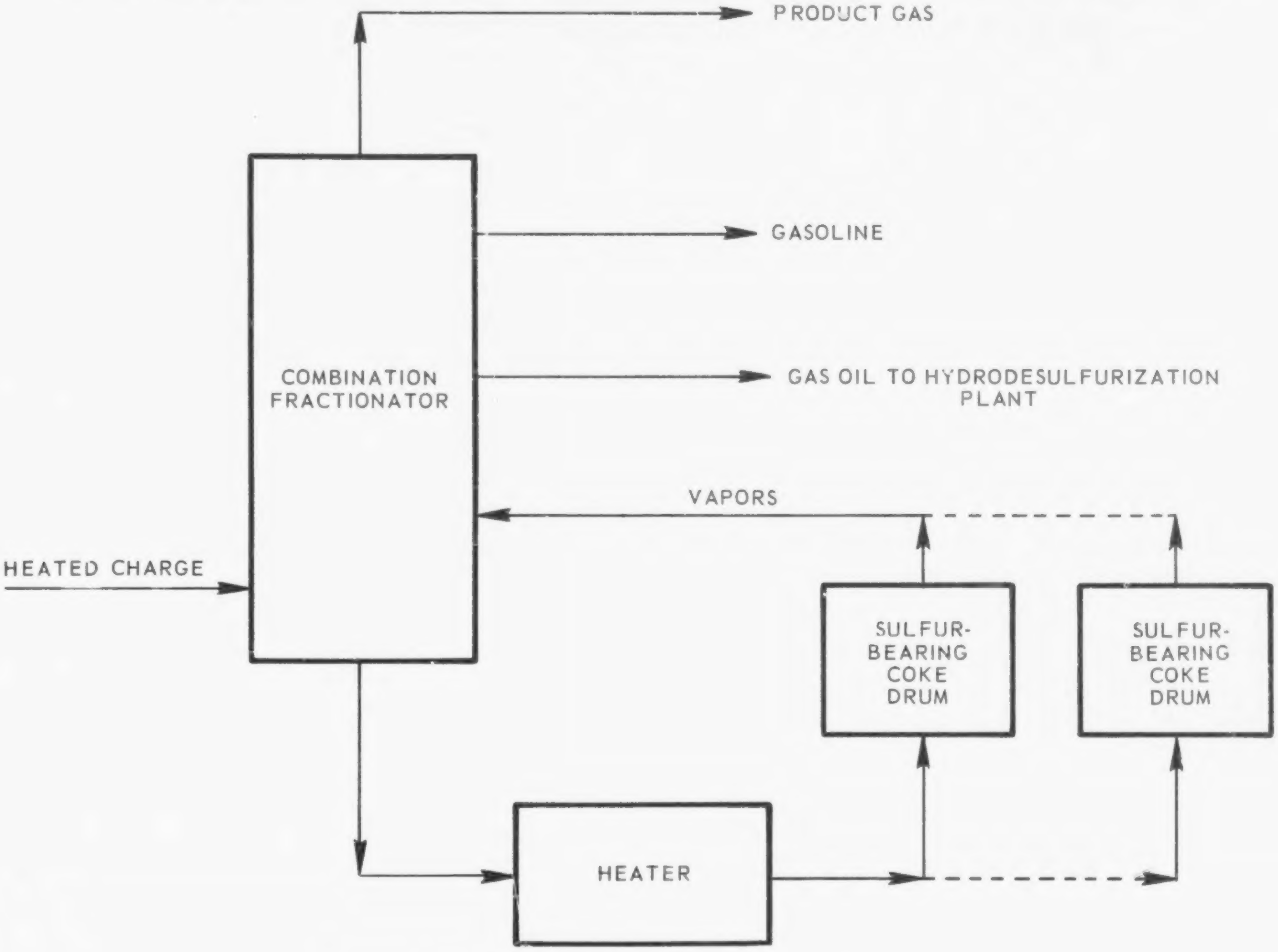

Figure 4-19. Delayed coking (simplified flow chart).

technique if the de-asphalted gas oil is hydrocracked and blended with high-sulfur, bottom fractions. The process is licensed by M. W. Kellogg Company, among others. Direct operating cost at a 5000-barrel-per-day plant is about $.25 per barrel.[74]

4.4.3.3 Cost Studies—Cost estimates of fuel oil desulfurization were prepared by Bechtel Corporation in 1964 for California crude[72] and in 1967 for Venezuelan crude,[73] and by Arthur G. McKee and Company in early 1968, for crudes processed in refineries in the United States.[70] The 1964 study, now largely outdated, is not discussed here.

In all processes involving hydrogen, a major cost item is the hydrogen. Low-cost sources and maximum use of hydrogen are of utmost economic importance. A cost estimate published in 1966 for a 50,000-barrel-per-day refinery processing Venezuelan crude and desulfurizing from 2.0 to 0.5 percent gave an operating cost of $.284 per barrel.[75] This was increased to $.424 per barrel when a 5-year payout after taxes was used.

1967 Bechtel Study—The specifications for the selected base case Caribbean refinery using Venezuelan crudes are given in Table 4–27.

A major assumption of the 1967 Bechtel report is that the product stream obtained from the refinery is fixed. Although in actual practice a refinery turns out those products

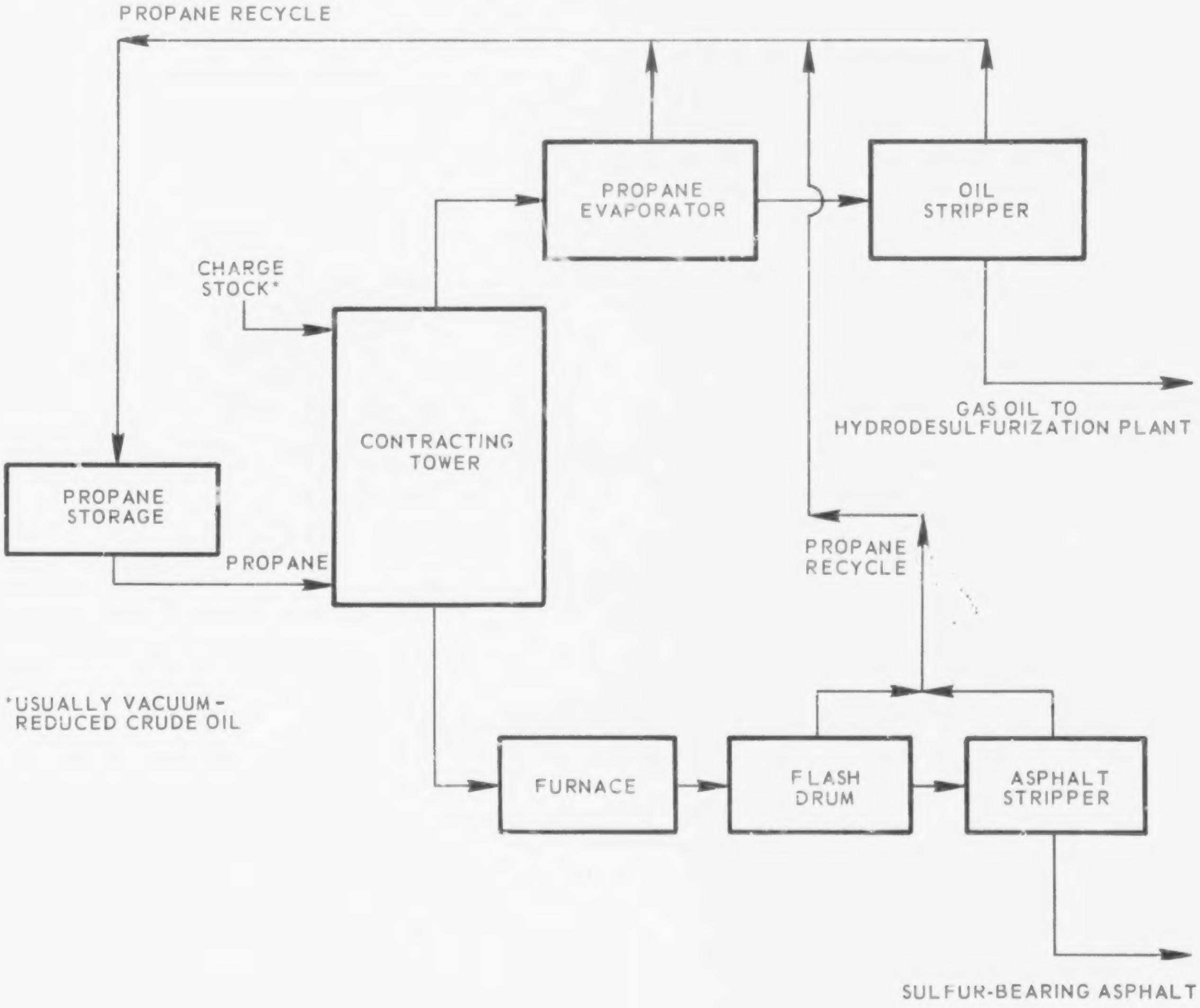
PROPANE RECYCLE
PROPANE EVAPORATOR
OIL STRIPPER
CHARGE STOCK*
CONTRACTING TOWER
GAS OIL TO HYDRODESULFURIZATION PLANT
PROPANE STORAGE
PROPANE
PROPANE RECYCLE
*USUALLY VACUUM-REDUCED CRUDE OIL
FURNACE
FLASH DRUM
ASPHALT STRIPPER
SULFUR-BEARING ASPHALT

Figure 4-20. Propane solvent de-asphalting (simplified flow chart).

Table 4–27. PROCESS SIZES AND YIELDS FOR 1967 BECHTEL STUDY [73]

Process	Size, barrels per stream day
Crude distillation	300,000 @ 23.6° API
Vacuum distillation	48,000
Catalytic cracking	23,000
Visbreaking	72,000
Alkylation	2,000
Lube plant	2,000

Product yield	Volume, percent of crude
Regular gasoline	8.1
Premium gasoline	4.1
JP–4	1.5
Jet A–1	1.5
Kerosene	4.2
No. 2 distillate fuel oil	11.3
Automotive diesel	2.6
Marine diesel	3.3
No. 6 fuel oil	57.4
Lube	0.7
Naptha	3.0
Fuel and Loss	2.3
	100.0

that have maximum economic value, the Bechtel study, as one of its constraints, maintained a fixed volume of lighter products. The value of low-sulfur residual fuel oil will depend on the quantity and value of other products produced. These points should be noted in any consideration of the results of this study. Table 4–28 is a summary of residual-fuel-oil quality and cost data for different processes at a typical Caribbean refinery.

Certain comments are in order regarding product and process capabilities. When the sulfur content is reduced to about 1.0 percent, the viscosity of the oil is reduced to the lowest limit of ASTM specifications for No. 6 fuel oil (45 SSF at 122°F). When the sulfur content is reduced to 0.5 percent, the viscosity reaches the lowest limit allowed by import regulations (145 SSU at 100°F). Residual fuel oils of relatively low sulfur content, down to about 0.87 percent, may be attained without charging the oil directly to a desulfurizer or having coke as a product for disposal. Fuels with a sulfur content of about 0.5 percent may be produced by direct residual desulfurization or by delayed coking and solvent de-asphalting followed by blending. Because of the high metal content of this crude oil, process capabilities and costs are less reliable for desulfurization below 0.87 percent.

The volumetric value of fuel oil decreases with desulfurization. This is illustrated in Figure 4–21, where degree of desulfurization is related to costs, calculated on 5-year-payout basis.

1968 McKee Study [70]—As the basis of the

Table 4–28. HEAVY FUEL OIL PRODUCT QUALITY AND INCREMENTAL COST [73]

	Sulfur wt percent	Viscosity [b]	Metals, ppm	Incremental operating cost [c]		Incremental facility investment
				5-yr payout	Break-even [d]	
Base case	2.6	170 SSF	500			$120,000,000 (1967 replacement cost)
Process: [a]						
Distillation	1.96	88 SSF	478	$0.24/bbl	$0.15/bbl	44,000,000
Delayed coking	1.14	145 SSU	265	0.58	0.40	88,000,000
Solvent de-asphalting	0.87	220 SSU	275	0.61	00.40	100,000,000
Solvent de-asphalting and coking	0.5	145 SSU	189	0.73	0.49	118,000,000
Solvent de-asphalting and residual desulfurization	0.52	145 SSU	23	1.02	0.65	154,000,000
Residual desulfurization	0.87	210 SSU	342	0.79	0.54	117,000,000

[a] All processes include optimized hydrogen treating.

[b] SSF at 122° F: SSU at 100° F.

[c] Value of undesulfurized residual fuel oil is $2.00 per barrel.

[d] Full depreciation over a 10-year period.

McKee study, an "average" refinery was selected for each of the five petroleum districts established in the United States by the Bureau of Mines. The crude used in each refinery was typical for its district, as reported by the Bureau of Mines. In the determination of size for the average refinery, the many small refineries in that district were neglected if they contributed only a small porportion of the production.

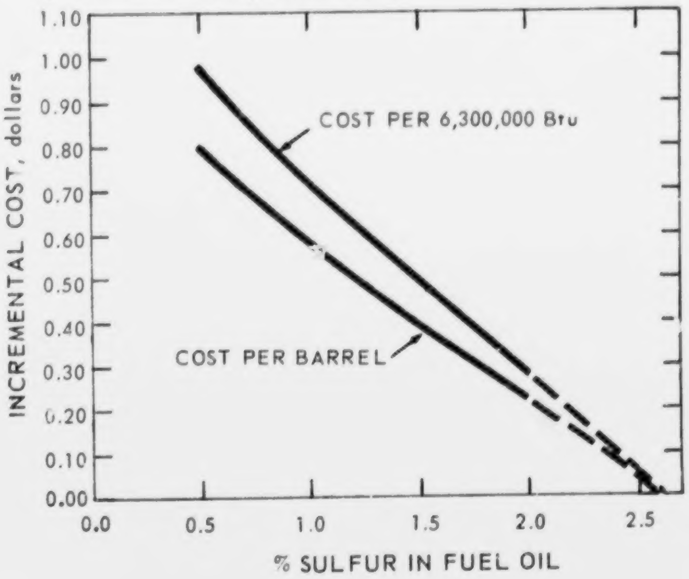

Figure 4-21. Incremental desulfurization costs - per barrel versus constant heating value.[73]

This study assumes that hydrodesulfurization will lead to an upgrading of products and that residual fuel oil will be partly upgraded to distillate fuel which can be sold. The major results when desulfurizing to 1.0 percent and to 0.5 percent are shown in Tables 4–29 and 4–30.

These data show the production of No. 6 fuel oil for the typical refinery without hydrodesulfurization in each district. A decreased amount of this fuel is produced when hydrodesulfurization is used, but some No. 2 fuel oil is also produced. In addition, sulfur is produced in the sulfur recovery plant. Operating costs include hydrogen production, H_2S and sulfur removal, and operation of the hydrodesulfurization unit itself. They do not include depreciation or charges on the capital investment. The decreased amount of No. 6 fuel oil produced is shown as a debit while the increased production of No. 2 fuel oil is credited to the operation as is the sulfur recovered.

The major conclusion to be drawn from this study is that, for a refinery of reasonable size, production of low-sulfur residual fuel oil may yield a net income on operation. The net profit, of course, would be larger if higher prices for low-sulfur residual oil were assumed. Disposal of the large amount of dis-

Table 4–29. PRODUCTION AND COST DATA FOR PRODUCING 1 PERCENT SULFUR RESIDUAL FUEL OIL FROM CRUDE OIL IN SPECIFIED DISTRICTS AT AN AVERAGE REFINERY[70]

	Petroleum district				
	1	2	3	4	5
Existing No. 6 fuel oil production for average refinery, bbl/day	11,340	—	—	2,810	18,631
No. 6 fuel oil production after process changes, bbl/day	9,350	—	—	2,250	16,470
Additional No. 2 fuel oil production after process changes, bbl/day	2,570	—	—	730	4,100
Additional sulfur produced, long tons/day	16.4	—	—	5.05	25.9
Capital investment, $\$10^6$	4.85	—	—	2.085	6.865
Operating cost, per day [a]	$ 4,327	—	—	$2,625	$ 5,627
No. 6 fuel oil debit	4,580	—	—	1,178	7,120
No. 2 fuel oil credit	10,800	—	—	2,760	14,620
Sulfur credit	533	—	—	164	844
Total operating cost per day	+$ 2,381	—	—	–$ 879	+$ 2,714

[a] Does not include depreciation or other capital charges.

tillate fuel oil may be a problem in some districts, and this fuel may have to be upgraded to meet specific requirements. This would affect the cost.

4.4.4 Gas

Many natural gases, as found, contain elemental sulfur and sulfur compounds. The sulfurous constituents may range in concentration from undetectable amounts to over 10 percent.

It is usually necessary to remove the sulfurous materials when they occur in other than trace concentrations. Elemental sulfur causes plugging of equipment. Hydrogen sulfide is a highly toxic material, even in very low concentrations. It causes rapid corrosion in steel when moisture is present or at elevated temperatures, and is very reactive with copper or copper-bearing materials under all conditions. Organic sulfur compounds (mercaptans, disulfides, carbonyl sulfide, thiophenes) are malodorous, corrosive, and generally undesirable in significant concentrations. Specifications for saleable natural gas generally call for the concentration of hydrogen sulfide to be below ¼ grain per 100 standard cubic feet of gas and total sulfur to be no more than 10 grains per 100 standard cubic feet.

Literally scores of methods are employed industrially to remove the sulfur-bearing materials from natural gas. The economical choice of process depends on factors such as quantity, temperature, pressure, and relative humidity of the gas; quantity and composition of sulfur; nature of other contaminants present; and desirability of recovering sulfur in elemental form as a by-product of treating.

Wet scrubbing methods are categorized as to whether they depend on chemical reaction of the treating agent with sulfur compounds or on selective solubility of the sulfur compounds.[76] Treating with dry materials can be categorized as methods that depend on chemical reaction and methods that depend on selective physical absorption.

Cost of desulfurizing natural gas depends on the many factors outlined above in discussion of methods. In general, the cost will range from a fraction of a cent to several cents per thousand standard cubic feet of gas.

4.5 FLUE GAS DESULFURIZATION

4.5.1 Introduction

Removing SO_2 from the flue gases is an obvious way of reducing SO_2 emissions. Flue-gas-desulfurization processes may provide

Table 4–30. PRODUCTION AND COST DATA FOR PRODUCING 0.5 PERCENT SULFUR RESIDUAL FUEL OIL FROM CRUDE OIL IN SPECIFIED DISTRICTS AT AN AVERAGE REFINERY[70]

	Petroleum district				
	1	2	3	4	5
Existing No. 6 fuel oil production for average refinery, bbl/day	11,340	4,630	5,600	2,810	18,631
No. 6 fuel oil production after process changes, bbl/day	7,940	3,710	4,480	1,910	13,220
Additional No. 2 fuel oil production after process changes, bbl/day	4,310	1,200	1,455	1,152	6,890
Additional sulfur produced, long tons/day	24.6	4.05	4.92	7.17	39.1
Capital investment, $\$10^6$	5.78	3.40	3.74	2.50	7.45
Operating cost, per day[a]	5,527	3,565	3,860	3,435	6,510
No. 6 fuel oil debit	7,825	1,485	2,240	1,890	12,150
No. 2 fuel oil credit	18,140	4,710	5,800	4,370	24,590
Sulfur recovery credit	800	130	160	234	1,295
Total operating cost/day	+$ 5,588	−$ 210	−$ 140	−$ 721	+$ 7,225

[a] Does not include depreciation or other capital charges.

an alternative method for large fuel consumers where a switch to a low-sulfur fuel may present technical and economic probbems.

It has been estimated that 28.6 million tons of SO_2 was emitted into the atmosphere in the continental United States in 1966. Of this total, about 13.1 million tons (45.5 percent) was the result of combustion of oil and coal in electric power generating plants.[77] Other combustion processes accounted for approximately 9.1 million tons (31.5 percent). Because of the predominance of fuel combustion as an SO_2 source, primary research and development emphasis has been placed on the development of processes and equipment for controlling this source. Many flue gas desulfurization processes have been proposed, and a number of them are currently being actively developed. One of these processes, the limestone injection-wet scrubbing process, is in full-scale preliminary operation, and other large-scale prototypes will be in operation within the next 3 years.

Progress in developing suitable flue-gas-desulfurization processes has been slow because of the magnitude and complexity of the problem. A modern power plant of 1000-megawatt capacity, burning coal with a sulfur content between 2.5 and 3 perecnt, will emit 1.7 million to 2 million cubic feet per minute of flue gas with an SO_2 concentration of between 0.2 and 0.3 percent by volume. Desulfurization of flue gas is further complicated by a wide variation in the size of power plants.

The technical and economic feasibility of most processes is closely related to plant size.

It is unlikely that a single flue-gas-desulfurization method will be developed that is capable of controlling effluents from all types of sources. Each of the several techniques now being studied demonstrates varying capabilities for controlling different aspects of the problem. The control technique to be used will depend on factors such as boiler size and configuration, age, load pattern, characteristics of the fuel, by-products, and geographical area (particularly with respect to ability to consume by-products).

The most promising SO_2 removal processes currently under investigation in the United States are limestone-dolomite injection, catalytic oxidation, and alkalized-alumina sorption. A potassium sulfite scrubbing system also is receiving increased attention. The limestone injection process, which appears to have potential for controlling emissions from both small and large sources, is, with certain variations, currently being installed on a number of boilers in the 125- to 700-megawatt range. The alkalized alumina and catalytic oxidation processes seem to be more applicable to large new units, since their integration into the power plant is required. Other "second generation" processes that show potential for improved economics and control capabilities also are being actively developed for installation during the years between 1975 and 1980. These systems may find application in the future as replacement processes for those now being developed, or in special circumstances where the economics of a particular system are justified.

4.5.2 Alkalized Alumina Process

4.5.2.1 Introduction—The alkalized alumina process is one of a number of flue-gas-desulfurization schemes that use a dry metal oxide to contact and absorb the SO_2 in a gas stream. Because the activated sodium aluminate sorbent is expensive, a regenerative process is employed and the sorbent is recycled. Sulfur is recovered in the regenerating process. Developers claim 90 percent recovery of SO_2 from the gas stream.

The process, which was developed with financial assistance from the Public Health Service, is patented by the Bureau of Mines, Department of the Interior. Their studies have progressed from a 92-cfm-at-625°F pilot plant erected in 1961 at the Pittsburgh Coal Research Center, Bruceton, Pennsylvania, to a recently installed plant rated at 0.2 megawatt or 920 cfm at 625°F. Both installations have transport reactors and use furnaces fired with pulverized coal to supply SO_2-bearing gas streams. To fill in gap areas where further fundamental data were needed for design studies, the National Air Pollution Control Administration (NAPCA) contracted with AVCO Space Systems Division to do kinetics work on sorption and regeneration and incorporate these data in mathematical process models for use in determining process costs as a function of design. W.R. Grace Company was given a contract to do extensive work to test the life of alkalized alumina, improve its physical and chemical properties, and determine the optimum means for producing a low-cost sorbent. Other studies were funded by the Bureau of Mines to do sorbent development and kinetic studies on regeneration.

The British have advanced the process development under the auspices of the Central Electricity Generating Board (CEGB).[75] A fluidized, large-diameter absorber-contactor is the foremost innovation of their "sodium aluminate" process. CEGB is ready to design, construct, and evaluate a 50-megawatt prototype plant.

The M.W. Kellogg Company has been selected by NAPCA as the prime contractor for process design and development, and will help determine whether a large, advanced-prototype plant is necessary to achieve optimum process efficiency and economics prior to incorporation of the process into a full-scale plant.

4.5.2.2 Process Description—The raw sorbent solid in the form of 1/16-inch spheres of dawsonite, $NaAl(CO_3)(OH_2)$, is activated at 1200°F to form high-porosity, high-surface-area sodium aluminate, which reacts with SO_2 in the flue gas at 300° to 650°F. The sodium aluminate reacts with SO_2 to form sodium sulfate, which is then regenerated in the presence of a reducing gas at 1200°F.

The basic steps in the process are shown in Figure 4–22. After leaving the boiler, the gases enter a dust collector and then a reactor, which removes the SO_2 from the flue gas at 600°F. Gas from the absorber then passes through an air preheater, a high-efficiency dust collector, and the stack. The spent sorbent is heated to between 1200° and 1300°F and enters the regenerator where it contacts a reducing gas (primarily H_2, CO, and CO_2), which is in the form of producer gas (gas from reforming of fuel oil or natural gas).

The sulfate-bearing pellet is regenerated to sodium aluminate and recycled. Hydrogen sulfide is the primary desorbed sulfur compound formed under reducing conditions in the regenerator. A conventional Claus unit (see Section 5.2) will be used to convert H_2S in the regenerator effluent gas stream to elemental sulfur.

The advantages of this process are:

1. It produces a highly desirable and valuable by-product, i.e., sulfur, which can be sold to offset process operating costs.

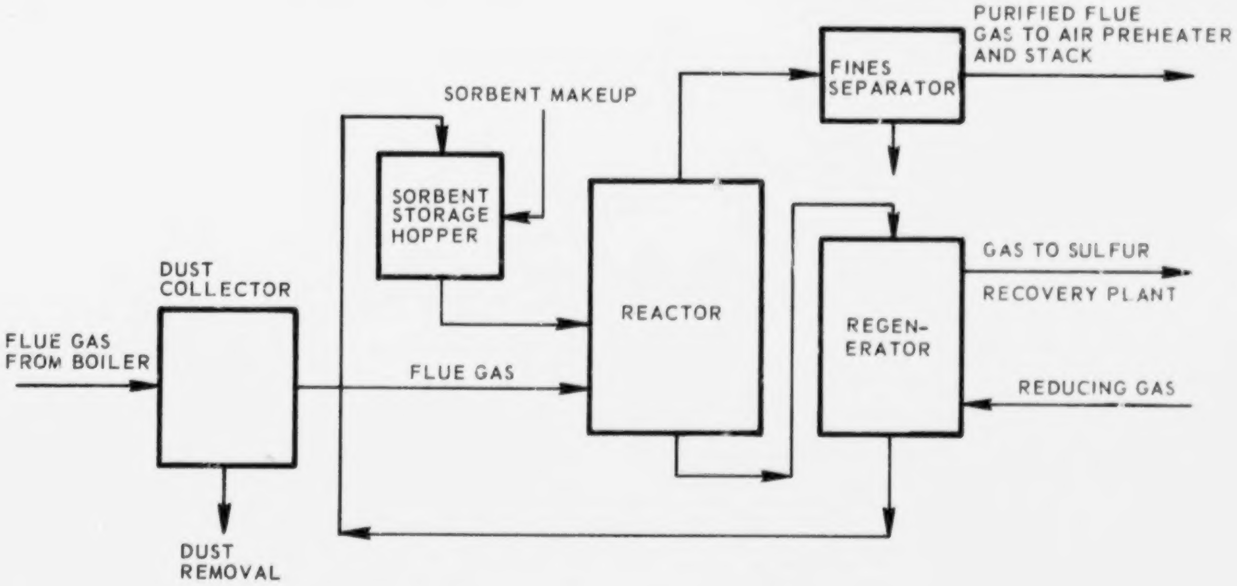

Figure 4-22. Alkalized alumina process.

2. The stack gases are released at a high enough temperature (250° to 300°F) to maintain buoyancy of the stack effluent.

Some of the disadvantages associated with this process are:

1. Sorbent make-up costs are high because of attrition.[79] Present sorbent cost is also high, but considerable progress being made in preparation techniques should reduce this cost. W.R. Grace's preliminary sorbent preparation work for NAPCA indicates that the CO_2-sodium aluminate process may be capable of producing sorbent for \$.20 per pound versus the \$.25 per pound projected earlier by the Bureau of Mines. Attrition is, however, a critical problem that must be overcome, perhaps by improving the sorbent or the design of the regenerating process.
2. The process is most applicable to new power stations.[80] To keep process costs at a reasonable level, lower SO_2 removal efficiency may have to be accepted for installations in existing power plants.
3. The overall process is large and complex, involving circulation of large amounts of sorbent at high temperature through the sorption and regeneration steps, production of reducing gas, and recovery of sulfur in a Claus unit.[81] This results in high capital charges for this SO_2 removal equipment.

4.5.2.3 Cost—Costs for the alkalized alumina process are difficult to estimate and are based on the assumption that a suitable sorbent will be available. It has, however, been estimated that for an 800-megawatt coal-fired plant incorporating a transport-dispersed-solids reactor, a capital cost of \$10.64 per kilowatt is required. The operating cost of such a unit would be about \$1.54 per ton of coal (60 mills per million Btu). These figures are based on the assumption that coal with a sulfur content of 3 percent and a 90-percent operating load factor will be used.[82] No allowance is made for revenue from by-product sale. If credit is taken for by-product sulfur, the operating costs would be decreased. These figures are also based on 0.1-percent attrition of the sorbent per cycle, which is considerably lower than the rates now experienced in a transport-type, dispersed-solids reactor; thus in all probability the actual operating costs would be higher.

On the other hand, use of a fluid-bed reactor may result in substantially lower sorbent make-up costs. An economic compromise for application to existing power plants might require acceptance of SO_2 removal efficiencies in the 50 to 80 percent range. Advances in regenerator design would result in lower process costs.

4.5.3 Limestone-Based Injection Process

4.5.3.1 Introduction—Oxides of sulfur produced by burning coal and oil can be reacted with the calcined products of limestone or dolomite to produce removable calcium-sulfur salts. Two basic limestone injection processes are currently being investigated, (1) limestone injected directly into the high-temperature zone of the boiler is calcined to lime and allowed to react with SO_2 in the flue gas and (2) limestone injected into the boiler is calcined to lime and subsequently becomes part of an aqueous SO_2 scrubbing solution in the scrubber. In the second process, the alkaline, milk-of-lime scrubbing solution reacts with SO_2 to form calcium and magnesium sulfites and sulfates, which can be collected for disposal. Both processes are of major interest because of their relatively low capital cost and because of their potential for being adapted to large and small, existing and new power plants. Their application will require little alteration of existing power plants. Because of these characteristics, the limestone-based processes are regarded as among the most promising SO_2 control methods.

4.5.3.2 Process Description—Dry Process—The first active program in the United States for the development of a dry limestone-injection process to control SO_2 from flue gas was initiated in 1964 by the Process Control Engineering Program of the NAPCA. Earlier work in Germany and Japan was inconclusive. A series of in-house and contract research projects to identify the important kinetic and process variables affecting the use of reactants and sulfur oxide removal efficiency was started. Results from these studies were incorporated into a conceptual design study of the dry-injection process conducted by the Tennessee Valley Authority as part of the NAPCA program for development of a large-scale prototype process. The flow chart for this prototype process, which will be operational in the summer of 1969, is shown in Figure 4–23. In this process limestone and/or dolomite is pulverized and fed into the high-temperature combustion zone of the furnace where it is calcined to the active oxide forms CaO and MgO.[83] The reaction of the additive with SO_2 and oxygen at temperatures above 1200°F forms gypsum ($CaSO_4$). Sulfates, unreacted lime, and fly ash are removed by conventional particulate collection equipment. Additional electrostatic precipitator capacity may, however, be required to maintain a given collection efficiency.

Wet Process—The principle of lime scrubbing was thoroughly studied in three separate but related programs in England in the 1930's. The first of these involved a 26,000-scfm-pilot-scale study. This work led to the construction of the still active Battersea SO_2 wet-scrubbing process in London. Sulfur oxide removal efficiencies of over 90 percent were obtained. A second pilot study was conducted at the Tir John Power Plant at Swansea, Wales. This process was reported to have demonstrated high SO_2 removal efficiency. This work led to the full-scale, cyclic lime process that was installed in the late 1930's on the Fulham power plant, where it operated

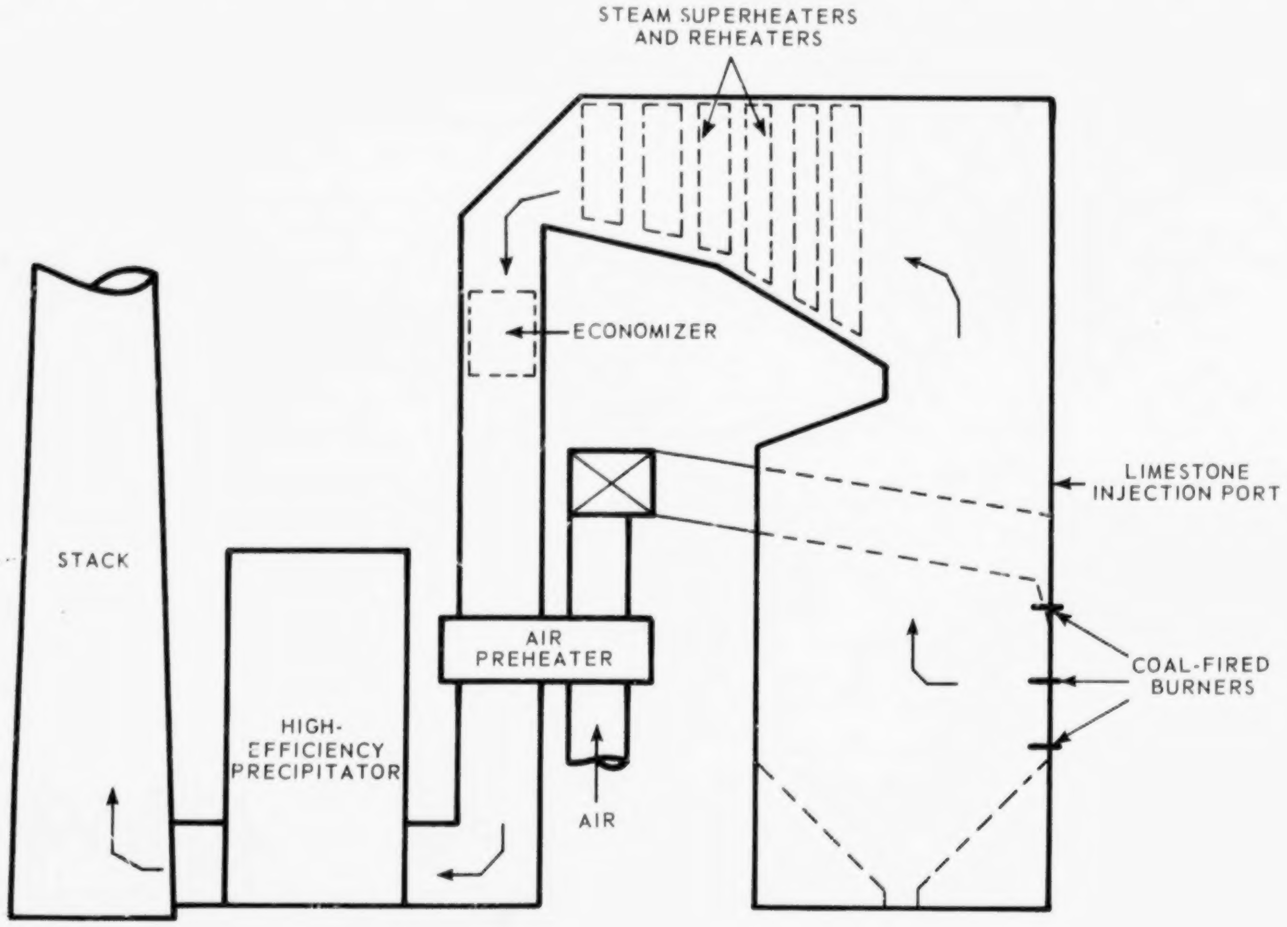

Figure 4-23. Limestone injection - dry process.

successfully until it was closed during World War II. These installations demonstrated the capability of the lime scrubbing process for removing SO_2 from flue gas. However, they also spotlighted specific process problems such as high maintenance and operating costs, low-temperature corrosion, solid wastes disposal, and loss of plume buoyance resulting in high localized ground-level concentrations of SO_2 and other emissions.

Unlike the earlier work done in England, the current limestone-injection lime-scrubbing process for SO_2 control is actually a combination of the two individual processes, (1) dry limestone injection directly into the furnace where it is calcined to lime and (2) scrubbing of the combustion flue gas by lime slurry for removal of SO_2. Figure 4–24 is a conceptual design for this process.

In the limestone scrubbing process, limestone is injected into the combustion zone of a boiler, where it is calcined to reactive lime. The lime and fly ash are collected by the scrubber, where the calcined limestone forms a slurry of reactive milk-of-lime, which reacts with the SO_2 in the flue gas to form sulfite and sulfate salts. The spent scrubber liquor and reaction products are allowed to settle. Ash and reacted lime are removed for disposal. Scrubber liquor is recycled to reduce water requirements and avoid water pollution.

The limestone-injection wet-scrubbing process for SO_2 control was first researched in the United States by Wisconsin Electric Company and Universal Oil Products Company in 1963 and 1964.[55] The Combustion Engineering Company in cooperation with Detroit Edison Company recently conducted research on a similar process, which involved injection of limestone and dolomite into a full-scale 170-megawatt boiler followed by a 2500-cfm scrubber processing about 1.0 percent of the total boiler flue gas. This work resulted in the purchase of the limestone-injection wet-scrubbing process for use on three full-scale power plant boilers in the 125- to 420-megawatt range. These installations have been sold

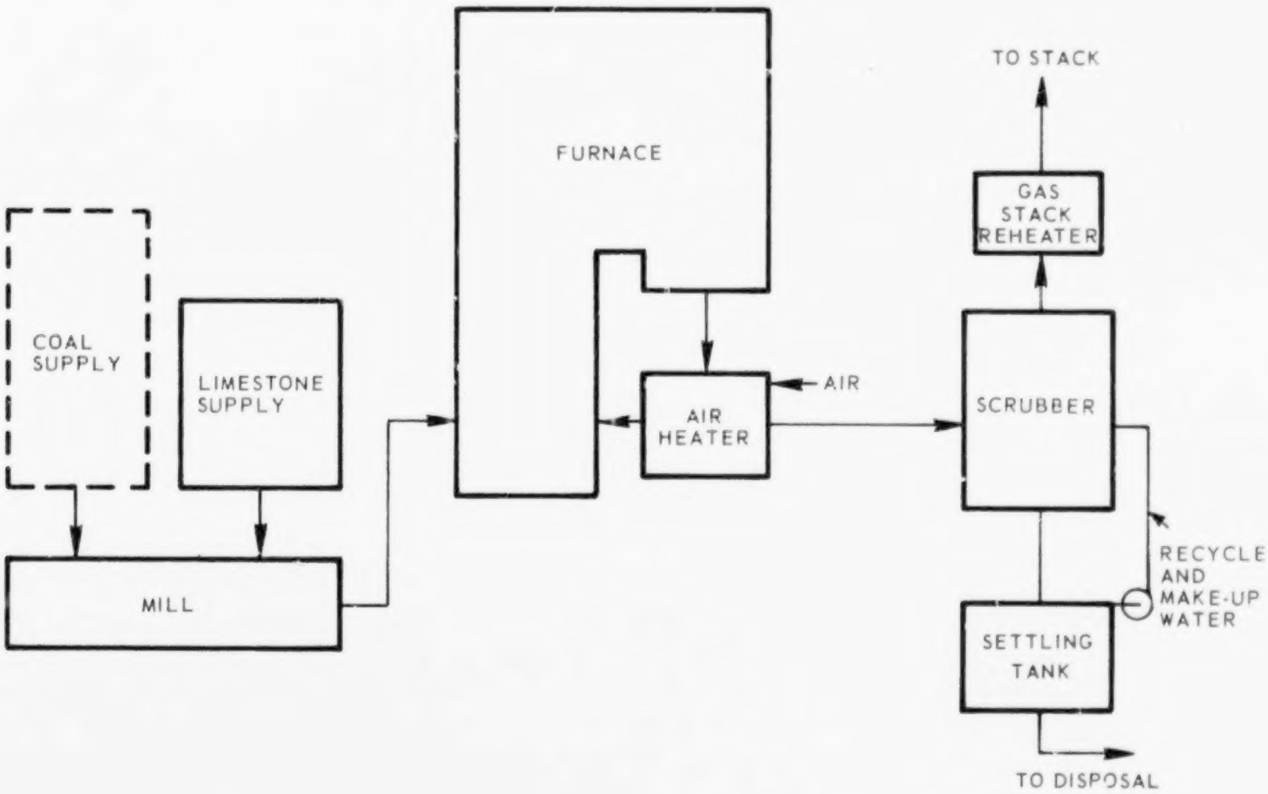

Figure 4-24. Limestone injection - wet scrubbing process.

with a guaranteed removal efficiency of more than 80 percent of SO_2 and 98 percent of particulates. One of these systems is currently in preliminary operation at the Union Electric Company's Meramec Plant in St. Louis.

4.5.3.3 Process Cost—Conceptual design and economic studies conducted by TVA under NAPCA contract indicate that the capital investment for the dry limestone injection process for an 800-megawatt power plant would be about $3 million and that the net operating cost when removing 40 to 60 percent of the SO_2 would be about $0.73 per ton.[55] These figures assume limestone delivered at $2.00 per ton, and 200 percent stoichiometric addition of limestone. Similar estimates of the capital and operating costs of the limestone-scrubbing process indicate that capital costs would be $4 million and operating costs would be $0.94 per ton of coal fired.[55] Operating cost estimates by the vendor (Combustion Engineering Co.) range from $0.35 to $0.50 per ton of coal ($0.015 to $0.02 per million Btu).[56]

4.5.3.4 Future Plans—A full-scale boiler (240-Mw) of the TVA power generating system is being equipped for direct injection of limestone and dolomite. This unit, at the Shawnee power plant, is expected to be placed on line in mid-1969. It is the purpose of these prototype studies to demonstrate process feasibility and generate economic and design data on the dry injection process.

Three large-scale limestone-scrubbing demonstration units have been sold by Combustion Engineering Company for installation on full-scale boilers. These units have been sold as guaranteed processes and are based on extrapolation of data gathered from small-scale pilot studies conducted jointly by Combustion Engineering and Detroit Edison.

An intermediate-scale applied research program will be initiated by NAPCA to provide the needed intermediate-scale data on prototype equipment to study engineering, kinetics, and economic problems associated with wet-scrubbing processes. Three scrubbers, each capable of scrubbing approximately 100,000 acfm, will be evaluated, and studies will be made of reaction and process kinetics, and factors such as high- and low-temperature corrosion, solid waste disposal, water pollution potential, and plume reheating.[51]

4.5.4 Catalytic Oxidation Process

4.5.4.1 Introduction—This process converts sulfur oxides to sulfuric acid by passing the flue gases over a vanadium pentoxide catalyst, which oxidizes the SO_2 to SO_3. The SO_3 then combines with water vapor in the flue gas to form sulfuric acid. Subsequent cooling condenses the acid.

In 1961, Bituminous Coal Research Incorporated (BCR) and Penelec (composed of Pennsylvania Electric Company, Monsanto Chemical Company, Research-Cottrell Incorporated, and Air Preheater Company) proceeded, independent of each other, to show the feasibility of sulfuric acid production on pilot-plant scales using similar methods. The BCR investigations were carried out at Monroeville, Pennsylvania, and the Penelec group worked at the Seward, Pennsylvania, power plant. The Penelec group's investigations have now advanced to an operating 12-megawatt prototype plant at Portland, Pennsylvania, which appears to be the most promising system using this process. This work has proved successful, and Monsanto has announced plans to market the process.

In Japan the Kiyoura-TIT process, another variation of the catalytic oxidation process, is being used; and a pilot-plant installation is operating in Omuta, Japan. This process involves the injection of gaseous ammonia to form the by-product, ammonium sulfate, $(NH_4)_2SO_4$. While TVA conceptual design studies considered using ammonium sulfate as an intermediate substance from which a phosphate fertilizer could be produced, current demand for $(NH_4)_2SO_4$ from this source is limited in this country because ample quantities are generated by the coke industry.[79]

4.5.4.2 Process Description—The catalytic oxidation process, as shown in Figure 4–25, is an adaptation of the contact catalytic process used in the manufacture of sulfuric acid. Many of the details of the process are not available because of the proprietary nature of this process.

A high-efficiency electrostatic precipitator

(99.5%) is employed to remove particulate matter before the gas enters the catalyst bed at elevated temperatures of 800° to 850°F. Sulfur trioxide formed in the catalyst bed reacts with water vapor in the flue gas to form sulfuric acid. In the BCR method, vapor condensation was carried out by two air-cooled tubular heat exchangers, which preheated the boiler combustion air and preheated boiler feed water. BCR reported that through careful temperature control of this arrangement higher acid concentrations are possible.[51] Monsanto achieved a reported 78 percent sulfuric acid strength by using a rotary air preheater. Condensation occurred both in the acid condenser and mist eliminator sections. Over 99 percent of the sulfuric acid formed is collected in these sections. The gas is exhausted through the stack at approximately 220°F.

A fixed-bed catalyst achieved 90 percent conversion of SO_2 to SO_3 on the first pilot plant; however, a means for cleaning the bed must be provided for use in a large plant to preserve the life of the catalyst and maintain high conversion efficiencies.[57] Even minute amounts of certain particulates, such as selenium, arsenic, or chlorides, deactivate vanadium pentoxide.

Corrosion properties of sulfuric acid are minimized when the concentration is above 93 percent; however, the weak acid vapors are extremely corrosive below their dew point, and special materials of construction are required on the cooler portions (below 500°F) of the equipment.

The advantages of this process are:

1. The SO_2 removal system is simple.
2. Recycling of catalyst is not required.
3. Effluent-stack-gas buoyancy is maintained.
4. The by-product acid may prove profitable in some areas.
5. All raw materials are contained in the flue gas.

Some of the disadvantages of the catalytic oxidation process are:

1. The need for expensive corrosion-resistant materials of construction in the cooler section.
2. Rearrangement of the gas stream through the boiler's economizer section is necessary in order to supply the converter with 850°F flue gas. Provision must be made to route the gases back to the economizer or place the economizer after the converter.
3. Marketability of 75 to 80 percent acid is questionable unless such markets as the steel or fertilizer industries are

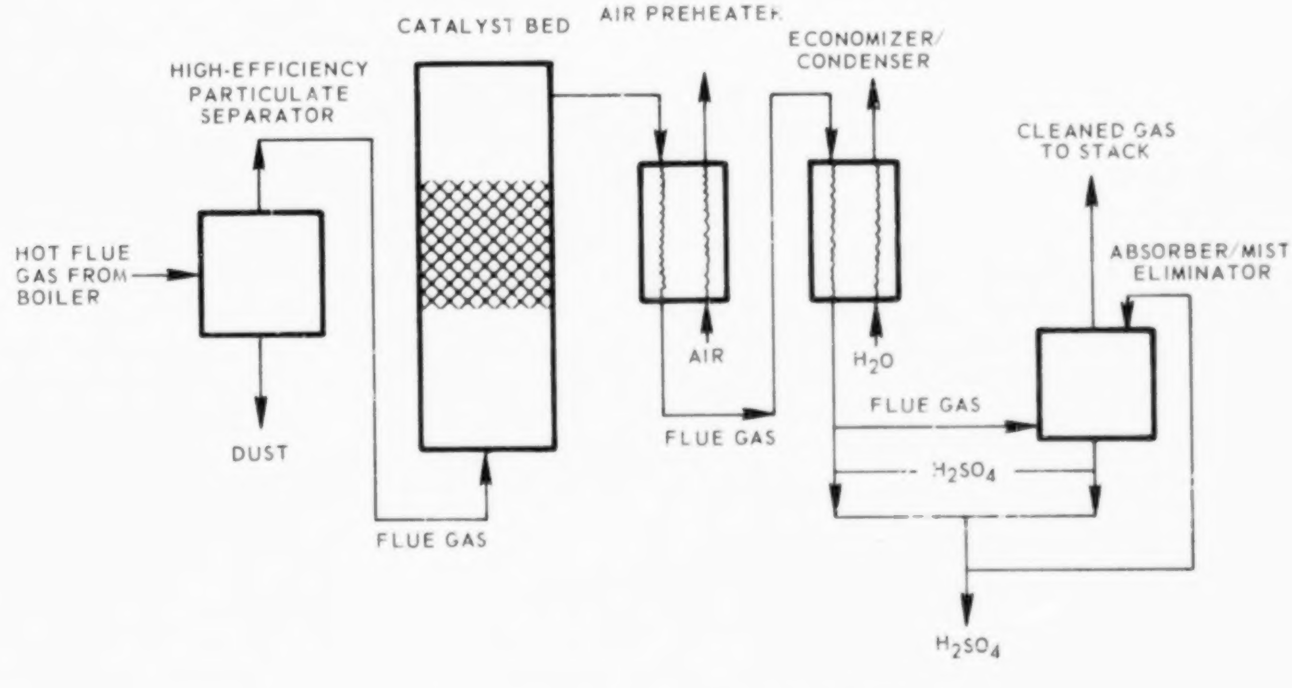

Figure 4-25. Catalytic oxidation process.

reasonably close to the supply of acid.

4. The process is difficult to apply to older plants because of the problems of tapping existing flue gas streams at a point where required temperatures exist.

4.5.4.3 Cost—Estimated installation cost for this process is \$20 to \$30 per kilowatt above that of a new conventional power station. The operating costs for an 800-megawatt plant have been estimated to be \$1.75 per ton of coal burned, without credit for the acid produced (0.613 mill kw-hr or 68.4 mill/million Btu).[72] If credit is taken for 78 percent acid by-product from a 3-percent coal, using a 90-percent recovery factor, \$1.06 per ton of coal fired might be realized (\$10 per ton is the estimated market value of the acid). The overall costs (or credits) associated with this process are dependent upon the sales value of the acid.

4.5.5 Beckwell SO_2 Recovery Process

4.5.5.1 Introduction—The Beckwell Process has been developed by the Wellman-Lord Co., a division of the Bechtel Corp. This process uses a potassium sulfite scrubbing solution and has been evaluated at the Gannon Station of the Tampa Electric Co. This pilot-study has led to the construction of a 56,500-cfm pilot plant scheduled for operation in April 1969 at the Crane Station of the Baltimore Gas & Electric Co.

4.5.5.2 Process Description—SO_2 is removed from the flue gas by scrubbing with a solution of potassium sulfite. The absorbed SO_2 forms potassium bisulfite, which precipitates out of solution as potassium pyrosulfite. Heating this potassium pyrosulfite converts it back to potassium sulfite, and a concentrated stream of SO_2 is recovered.[88] This SO_2 may be recovered in the anhydrous form.

4.5.5.3 Process Cost—For a 500-megawatt coal-fired power plant, it is estimated that installed costs will be in the range of \$5 to \$6 million. Net operating costs will depend largely on the price received for the recovered SO_2; however, a breakeven cost is envisioned.[88]

4.5.6 Other Processes

4.5.6.1 Introduction—The four processes previously mentioned (alkalized-alumina sorption, wet or dry limestone-dolomite injection, potassium sulfite scrubbing, and catalytic oxidation) are the main processes developed to the large pilot-plant stage, prototype scale-up, or full-scale plant installation in the United States. There are between 60 and 70 other SO_2 removal systems that are in various stages of development.

4.5.6.2 Process Descriptions—In inorganic-solids sorption systems (excluding metal oxides), the dry system approach is typified by the Reinluft process.[79] A small-scale pilot plant is being operated in Warren Spring, England, by the Central Electricity Research Laboratory. Two larger-scale coal-fired pilot plants (10 megawatt) are operating in the Ruhr Valley, Germany. Available information indicates that carbon catalyst oxidation is igniting char in the absorber. Evaluations must be held in abeyance, however, because the owners of these German units have made process details inaccessible.

Basically, flue gas containing SO_2 is passed through a bed of activated char at temperatures of 200° to 300° F. During adsorption, SO_2 is oxidized to SO_3, which reacts with flue gas moisture, yielding H_2SO_4. The char adsorbent is removed to a regenerator and heated to 750° F, liberating SO_2 and CO_2. A conventional acid plant converts SO_2 into concentrated acid. An efficiency rate of 95 percent is claimed. It is estimated that, for the comparable 800-megawatt power plant burning 3-percent-sulfur coal, a \$14,217,000 capital investment is required. Operating cost, including 14 percent capital charge of total investment for 90-percent load factor, is \$5,431,000 per year (0.857 mill per kilowatt-hour, or \$2.45 per ton of coal).[82]

Some advantages of this system are: (1) production of a desirable concentrated acid, (2) adequate buoyancy of discharged stack gasses, and (3) the regenerator's self-activation of the charcoal. At present, however, the disadvantages seriously impair the system's promise. The disadvantages are: (1) susceptibility to fires in the absorber, due in part to the fact that the char becomes activated to a higher degree with each subsequent desorption; (2) necessity for large amounts of char; and (3) high cost of materials and recirculation.

The Lurgi process is a wet-char system that first cools the boiler gas by contact with a weak solution of sulfuric acid.[79] After adsorption of converted SO_3 by the char, water is intermittently sprayed into the gas stream to remove acid. Some of the disadvantages of this process are: weak recovered acid, cool effluent gases, and the need for corrosion-resistant materials of construction. The process has been tested in conjunction with chemical plant operations. Plans call for testing on a coal-fired power plant.

A similar wet-char process (removal of acid with wash water) is the pilot-plant operation of Hitachi, Ltd., of Tokyo.[79] A 2-kilowatt plant has operated at the Goi Power Plant, and a 50-kilowatt installation is being planned. The Japanese government subsidizes this work. Gas contact with carbon is done in a cyclic system employing six towers with alternating schedules for 30-hour uncooled gas adsorption, 10-hour washing, and 20-hour stackgas drying periods. The product acid of 10 to 15 percent is obtained by successively weaker washes of adsorption tower carbon. Increase in cost due to a required damper system to change the flow from tower to tower is a disadvantage.

Metal-oxide sorption systems—Besides alkalized-alumina and dolomite-injection systems, sorption with metal oxides is also being investigated.

The Grillo Process uses a slurry of manganese and magnesium oxide as an absorbent.[79] There are two series reactors, the first at a temperature of 248° to 302°F and the second ranging from 104° to 176°F. The gas stream is cooled by evaporation of absorbent slurry. After absorption, the regeneration of the absorbent is carried out by heating a mixture of $MgSO_4$ and coke in a Herreshoff-type furnace at 1470° to 1560°F. Concentrated SO_2 is evolved for sulfuric acid production. The ash and regenerated oxide are separated, the oxide suspended, and the slurry recycled.

The advantages are the use of carbon steel construction, non-attrition of absorbent, and and rapid absorption. The disadvantages are some fly ash generation, cooling of discharged gases, and pressure drops through the reactors. A small-scale pilot plant is operating. Costs have been estimated at $0.75 to $1.20 per ton of fuel for a 300-megawatt plant.

The Carl Still Process was developed by the Firma Carl Still and is being currently tested on a 10-megawatt unit at the Herne Power Station, Recklinghausen, Germany.[79] A brown coal (lignite) ash is reacted at 300°F after the SO_2-laden flue gas leaves the air preheater and before it reaches the control precipitator. The lime content of the lignite ash is 40 to 50 percent. After reaction with the flue gases, the spent absorbent can be discarded or the calcium sulfite can be heated to evolve a rich SO_2 stream for sulfuric acid production.

Three series reactors are used and the feed is recycled. The recycle-to-feed ratio is about 2 or 3 to 1. The major obstacles to this process appear to be that a suitable lignite is not widely available and formation of calcium sulfate would interfere with the activity of the basic ash in recycle. Costs for the process have not yet been determined.

Inorganic-liquid sorption systems—A molten-carbonate process is being developed to scrub SO_2 from the flue gas, using a eutectic mixture of $LiCO_3$, Na_2CO_3, and K_2CO_3 (with a melting point of 746°F) at about 800°F. The mass transfer of a liquid-gas system should be excellent; and, with the high temperatures obtained before the economizer, high reaction rates are possible. Elemental sulfur is the by-product. Bench-scale studies have shown that the carbonates are corrosive and that corrosion-resistant materials of construction are required. Regeneration appears difficult since reduction rates of sulfite and sulfate to sulfide are slow until temperatures of about 1150°F are reached. This accentuates the corrosion problem. In existing plants, access to the flue gas at 800°F is often complicated.

This system requires much less liquid compared to aqueous systems. The process does not cool the gas stream or add water to it. There is also some indication that the molten salt can control nitrogen oxides.

Aqueous-solution sorption systems—Besides the alkali-solids injection system with wet scrubbing, which was previously discussed, numerous processes have been devised to remove SO_2 from flue gases by scrubbing with water solutions. Prior to 1940, nonrecovery-type lime-water scrubbers were installed in England.

In the Battersea-Bankside power plants, flue gases were scrubbed with a solution formed by adding chalk to the alkaline Thames River water.[86] This process was developed in the 1930's by the British Electrical Authority. The operating cost to attain 90 percent removal of SO_2 was $1.15 per ton of coal, or 12 percent of the delivered coal cost. Capital costs of up to $3 million for this system were estimated for a 120-megawatt power plant.

Also in the 1930's the Howden-ICI Process used lime or chalk in water to scrub flue gases.[86] Holdup tanks caused the calcium sulfate to accumulate before the liquid was recycled. Operating costs were estimated in 1956 by U.S. Bureau of Mines to be $1.25 to $1.93 per ton of coal. One plant in England and one in Wales had generating capacities of 120 megawatts each.

Chemico is also studying a variety of water-based alkali scrubbing solutions for removing SO_2. Pilot-scale tests are currently under way with SO_2 removal efficiencies in excess of 90 percent. A pressure drop of 5 to 6 inches of water occurs across the scrubber.

Miscellaneous processes—Many other wet processes are being investigated. Among the names and systems encountered are Mitsubishi Shipbuilding Engineering Company, U. S. Stoneware Incorporated, the Cominco Ammonia Processes, and the Ionics/Stone & Webster Caustic Scrubbing Process. Despite the long history of wet scrubbing programs, many basic questions remain unanswered, and modern technology is being applied to solve them. The economics of these processes are being evaluated to determine by-product and plume-reheating costs.

Reduction of SO_2 to sulfur (the most marketable by-product) is another desulfurization process under active investigation. Princeton Chemical Research, Inc., is performing bench-scale studies on the catalyzed reduction of SO_2 by H_2S produced from sulfur and methane. The use of organic sorbents, both liquid and solid, is also under active investigation. Uniroyal is studying fibers, which may be developed to the extent that they could be used in processes capable of controlling SO_2 and particulates. Physical methods of separation are also under active investigation.

4.5.7 Systems for Small Sources

In a recent preliminary study a 600-gallon-per-minute recycling scrubber system was used to remove SO_2 from the flue gases of a 200,000-pound-per-hour industrial boiler.[89] The installation cost for such a system was estimated at $125,000. The scrubber's adsorbent slurry might be composed of sea water, limestone, soda ash, or any combination of these. Efficiencies for SO_2 removal could range from 70 to 99 percent. If such a system were adopted, the suggestion has been made that perhaps as much as 25 percent of the flue gas stream should bypass the scrubber and be added to the treated gases after SO_2 removal. This would elevate the stack gas exhaust temperature to about 50°F above the dew point to provide the buoyancy needed for dispersal and prevention of steam plume formation.

An installed cost of $750,000 and an operating cost of 0.3 mill/kw-hr were recently estimated for the limestone/dolomite wet process for an existing 250,000-pounds-of-steam-per-hour boiler.[90]

Scrubbers attached to small municipal and industrial boilers in the past have been used primarily to remove particulate matter. They have also been used on boiler gases for the recovery of CO_2 for making liquid CO_2 and dry ice.

4.6 COMBUSTION PROCESS MODIFICATIONS

4.6.1 Heat Recovery

One important means of reducing SO_2 emissions from fuel combustion systems is to increase the efficiency of the systems so that they use less fuel to produce a given amount of energy. Process improvements usually result in relatively small increases in efficiency; but when such improvements are applied to a large plant, fuel savings become immediately apparent. Since fuel combustion in power plants is the largest source of SO_2 emissions, this discussion is restricted to power plants.

Over the years, generation of electricity in large central stations has become steadily more efficient. Large modern steam-electric plants use approximately 8500 Btu to produce one kilowatt-hour of electricity. Many older, smaller plants still in operation require over 10,000 Btu to produce a single kilowatt-hour of electricity.

Improvements in the operation of power plant components can reduce the heat rate, or Btu/kilowatt-hour ratio, and thus save fuel and reduce SO_2 emissions. Small heat-rate reductions may result from:

1. Washing turbine blades.
2. Adjusting turbine control valves to insure proper lift.
3. Adjusting for maximum turbine throttle pressure.
4. Adjusting preheater seals and feedwater heaters.
5. Periodic cleaning of condensers.
6. Periodic cleaning of secondary and reheat superheaters.

In a recently cited case, the net result of these operations was a reduction in heat rate of about 45 Btu per kilowatt-hour.[91]

Another consideration in process efficiency is the steam generator itself. A reduction in heat rate results from increased boiler steam pressure and temperature. The effect on efficiency can be gauged from the rule of thumb that doubling the steam drum pressure produces a 7-percent decrease in heat rate. At present, a maximum steam pressure of 5000 pounds per square inch (gauge) is being achieved. Net heat rate has improved by 3 to 3.5 percent as main steam temperatures have risen from 900° to over 1000°F. Further gains should accompany advances in the design and fabrication of critical heat-absorbing surfaces such as firebox walls and convection zones. Modern fuel-feed systems, which provide proper fuel size and distribution, also contribute to overall efficiency.

Efficient boiler operation requires that the optimum air-to-fuel ratio be maintained. Control of fuel and air is automatic on all large modern boilers. Plant efficiency also improves with increasing unit size, as shown in Figure 4–26.[92] Heat rates below 8,000 Btu per kilowatt-hour have, however, not yet been sustained.

4.6.2 Improving Generating System Efficiency

Uniform electrical demand would be ideal for power plant operations; however, varying power demands call for flexibility in power generation. Flexible electrical production systems minimize the inefficient fuel use associated with startup, low-load, and cyclic operations of large boilers and thereby decrease SO_2 emissions.

Diesel and gas turbine generators are being installed at many generating stations to meet peak demands. These units, available in many sizes up to about 25 megawatts each, can reach full load very rapidly from a cold start. They are especially useful in systems with rapid load fluctuations since they can take up these fluctuations and allow the larger boilers to run at a constant, efficient rate. Because such units burn light fuel oils or natural gas, they do not emit large quantities of SO_2.

Another means of attaining system flexibility is the pumped-storage technique. During periods of low power demand, excess generating capacity is used to pump water to an elevated reservoir. Then, during peak demand periods, the potential energy of the water can be converted to electricity by a conventional hydroelectric plant. By this method, stored energy can be put on line in a few minutes. This method is practical only where terrain, water supply, and market conditions are suitable. In addition, considerable energy is lost in the pumping operation. In order to provide an overall SO_2 reduction, the

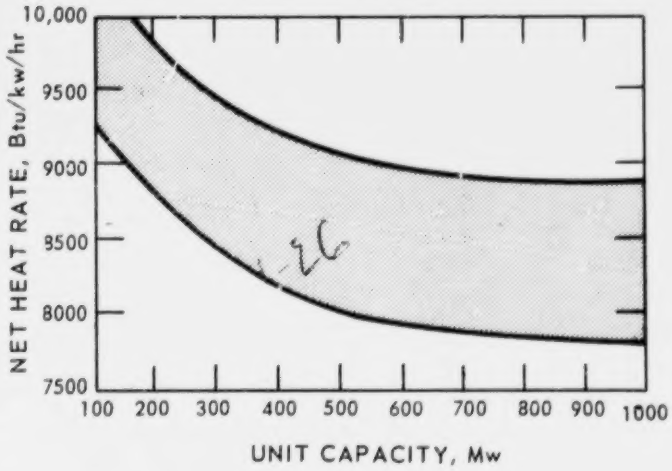

Figure 4-26. Comparison of plant size and heat rate.92

electricity used to pump water to the elevated reservoir must be provided by a nuclear plant, or a thermal plant burning a low-sulfur fuel.

Extra-high-voltage transmission networks also provide system flexibility by allowing utilities in one area to provide power to cities hundreds of miles away.

4.6.3 Newer Concepts of Central Station Power Generation

Greater process efficiency also can be achieved by changes in the basic techniques used to generate electricity. The following alternative methods of power generation represent techniques that are still in the developmental stage, but offer considerable potential efficiency would be about 1 percent, which advantages over present methods in that they use less fuel for a given electrical output and thus emit less SO_2.

4.6.3.1 High-Pressure Combustion[93, 94]—The design of a pressurized coal-fired furnace requires a new method of fuel burning, such as a fluidized-bed technique. In addition to providing for easier effluent removal, fluidized-bed carbonization is a potentially low-cost method of processing coal to obtain a gas stream capable of powering a high-temperature gas turbine. This high temperature offers a modest but significant increase in overall efficiency, which would produce a proportional reduction in SO_2 emissions. As shown in Table 4-31, for a 500-megawatt plant of this design, the expected increase in efficiency would be about 1 percent, which would result in a reduction in SO_2 emissions of 6.0 tons per day. This 1 percent efficiency increase could save about $196,000 per year in fuel costs. Although there are still many technical problems, the feasibility of fluidized-bed carbonization over a wide range of coal banks has been demonstrated.

4.6.3.2 Two-Step Combustion—This approach uses a two-stage process in which a first gasification stage yields concentrated fuel gas containing H_2S. The H_2S can be easily removed and converted into elemental sulfur, and the resulting sulfur-free fuel gas burned in a second combustion step.

The object is to balance the higher capital cost of this station against the lower operating cost which results from sulfur revenue and fuel savings. As shown in Table 4–31, the probable capital cost for a 500-megawatt clean power plant is about 20 percent more than for a conventional plant, or approximately $135 per kilowatt.[93] The expected 2-percent efficiency increase would mean an annual fuel savings of about $393,000. Sulfur dioxide emissions would be reduced by about 12.5 tons per day.

4.6.3.3 Magnetohydrodynamics[95]—Another new concept involves the use of a magnetohydrodynamic (MHD) generator as the first step in power generation, or an MHD "topping plant" combined with a conventional steam "bottoming plant." Basically, MHD is a technique in which the thermal energy of a hot gas is converted first to kinetic energy

Table 4–31. ESTIMATED EFFECT OF INCREASED GENERATING EFFICIENCY ON SO_2 EMISSIONS AND FUEL COST FOR 500-MEGAWATT PLANT

Combustion concept	Initial capital cost, dollars/kw	Overall efficiency, percent	Potential SO_2 reduction,[a] Tons/day	Potential SO_2 reduction,[a] Percent	Fuel savings, dollars/yr [b]
Conventional	112	39	—	—	—
One-step pressurized	NA [c]	40	6.0	2.5	196,600
Two-step	135 [d]	41	12.5	5.0	393,000
MHD	130 [d]	50	55.0	22.0	1,730,000
EGD	91 [d]	45	33.5	13.0	1,050,000

[a] Based on use rate of 4200 tons of coal per day, 3 percent sulfur content, 12,500 Btu per pound.

[b] Based on coal cost of $0.25 per 10^6 Btu and 300 days of operation per year.

[c] NA—not available.

[d] Cost presently speculative.

and then directly to electricity by the mass interaction of an electromagnetic field with the hot, rapidly moving, electrically conductive gas.

It is foreseeable that the thermodynamic efficiency of MHD conversion of fuel to electrical energy will ultimately reach 50 percent or even higher. This relatively high efficiency will allow much more effective use of fuel and, therefore, reduce SO_2 emissions as shown in Table 4–31.

Assessment of the capital costs of MHD steam power plants is difficult. Present indications are that capital costs for an MHD plant will be about $130 per kilowatt. Further intensive development, however, may lead to reduced capital costs.

Although direct conversion of thermal energy to electrical energy by MHD is appealing, the physical problems are formidable. One must cope with gas temperatures in the range of 4500° to 5500°F and with the slagging, corrosive, and erosive effects of mineral matter in the fuel. If existing problems are overcome, the MHD system, with its higher efficiencies, promises more effective use of resources and an opportunity for better control of the effluent-gas SO_2.

The first practical application of the MHD generator is being tested at the Air Force's Arnold Engineering Development Center in Tennessee. This device, using a treated coal at present, has a maximum operating time of only 120 seconds. It also has a potential for high nitrogen oxide emissions.

4.6.3.4 Electrogasdynamics—Electrogasdynamics (EGD),like MHD, is a direct energy conversion technique in which the kinetic energy of a flowing gas is directly converted into low-amperage, high-voltage electricity. In this process, positive ions are formed on the particles in the coal combustion gases by means of a corona discharge. These charged dust particles are carried downstream to the collector electrodes, where they build up an electrical charge, which flows through an external load. Current is forced through the load resistance as the gas does work in pushing the charged electric field in the generator.[96]

The primary advantages of an EGD coal-fired station are that it can operate at high efficiency and can be built at a low capital cost. These advantages result from the simplicity of the EGD system compared to conventional stations.

Preliminary studies, while rather speculative, indicate, as shown in Table 4–31, that EGD systems (approximately 500-Mw) can be built at a capital cost of $91 per kilowatt and can operate at an efficiency of 45 percent or higher.[97] A substantial decrease in air pollution would be obtained because the amount of effluent gas is reduced in direct proportion to the efficiency increase. For a 500-megawatt plant, an increase in efficiency of 6 percent (39 percent for a conventional plant—projected 45 percent for an EGD plant) will result in an emission reduction of approximately 33.5 tons of SO_2 per day and in fuel savings of about $1,050,000 per year, as shown in Table 4–31.

So far, no fundamental arguments against the feasibility of EGD coal-fired plants have been raised. However, there still remain many difficult engineering problems such as better ion sources, a better understanding of the mobility of charged particles, and new ways to match load impedances of the generator and the load. If all technical difficulties can be overcome, this process will have the potential of generating cheaper electricity at a smaller capital cost, and with some reduction in SO_2 emissions. At present, experiments are being conducted under contract with the Office of Coal Research of the Department of the Interior. A pilot-plant EGD power station is planned for 1972 or 1973. As with the MHD technique, the EGD has a potential for high nitrogen oxide emissions.

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5. INDUSTRIAL PROCESS SOURCES

5.1 NONFERROUS PRIMARY SMELTERS

5.1.1 Introduction

Several important metallic ores are found as sulfides, and the smelting of these ores produces SO_2. These ores include the sulfides of copper, lead, zinc, nickel, mercury, and molybdenum. In the United States, only the sulfide ores of copper, lead, and zinc are mined in appreciable quantity. Molybdenum also occurs as the disulfide, but current primary production of this metal in the United States is less than 50,000 tons per year, mostly from Colorado.

In 1966, nonferrous smelters emitted about 12 percent of the total estimated SO_2 emissions in the United States.[1] Production and SO_2 emissions data for that year are shown in Table 5–1.

Table 5–1. NONFERROUS SMELTER PRODUCTION AND SO_2 EMISSIONS IN 1966[1,2]
(TONS)

Metal	Concentrate	Metal production	SO_2 recovered	SO_2 emitted
Copper	6,008,000	1,581,000	996,000	2,830,000
Lead	790,000	441,000	11,700	146,000
Zinc	2,062,000	1,025,000	817,400	509,000
			1,825,100	3,485,000

Metal ores, as they occur in nature, are usually mixed with large amounts of worthless rock, which must be removed from the desired minerals. The nature of this preconcentration operation is defined by the characteristics of each particular ore. Among the principles of separation commonly employed are gravity separation, preferential wetting, flotation, and tabling. These methods depend upon such factors as relative density and wettability of mineral and rock. Because concentration produces a feed material of relatively high sulfur content, SO_2 concentrations from smelting operations are relatively high compared with those from fuel combustion. Smelter gases containing more than 3 percent SO_2 by volume can usually be fed to sulfuric acid manufacturing plants for conversion of the sulfur oxides into sulfuric acid. Of the 35 sulfide ore smelters in the United States, 17 plants (handling about 42 percent of the concentrate processed) are currently recovering some sulfur as SO_2 or sulfuric acid.[1]

The costs of controlling SO_2 emission from smelters is partly offset by the value of the sulfuric acid produced.

5.1.2 Copper Smelter Emissions Control

An important sulfide ore of copper is chalcopyrite ($CuFeS_2$). Such an ore is concentrated by suitable mechancial operations. Typically, the ore is crushed, ground, and thickened. The thickener underflow is then sent to water flotation cells, where frothing agents are added to produce foam and where "collector" materials such as xanthates are added to aid in the separation of chalcopyrite from rock. The copper mineral, along with water and other materials, forms a froth, which is drawn off and filtered.

The copper concentrate is then fed into a reverberatory furnance (Figure 5–1). The furnace is also charged with slag from the copper converter and with limestone and silicious fluxes. Hot combustion gases from the firing of gas, oil, or powdered coal pass directly over the charge. Some oxides of sulfur are emitted, but the principal products are copper matte: mainly cuprous sulfide (CuS_2), ferrous sulfide (FeS), and small amounts of other sulfides.

The purpose of the reverberatory furnace is to make copper matte and to form a slag to remove part of the iron.

An alternative procedure is to roast the copper concentrates in a vertical, multiple-hearth furnace before charging to the smelting furnaces. Sulfur dioxide constitutes 12 to 14 percent by volume of the gaseous emissions. The purpose of sulfur removal by roasting is to reduce the amount of sulfur to that required for subsequent operations. Many smelters omit roasting now, but it may return to general use as an air pollution reduction measure because high SO_2 concentrations favor the recovery of sulfur.

In addition to copper, the concentrate usually contains various other minerals and metals. Slag formed in the reverberatory furnace removes part of the iron. The matte dissolves precious metals and other metals such as bismuth and nickel, most of which are recovered later in the refining process. Part of the sulfur is driven off. Gases from the reverberatory furnace contain 1 to 2 percent SO_2 by volume and represent 25 to 40 percent of the sulfur present in the raw ore.[3]

The product of the reverberatory furnace is charged as a liquid to a copper converter, which is a cylindrical, refractory-lined vessel (Figure 5–1) containing numerous tuyeres. Air is blown through these tuyeres into the copper matte, forming blister copper and liberating the sulfur as SO_2.

$$Cu_2S + O_2 \longrightarrow 2\,Cu + SO_2$$
$$FeS + 3/2\,O_2 \longrightarrow FeO + SO_2$$

A silicious flux is added to combine with the FeO to form a slag; this slag contains so much copper that it is returned to the reverberatory furnace. The converter operations are not continuous, but consist of at least three

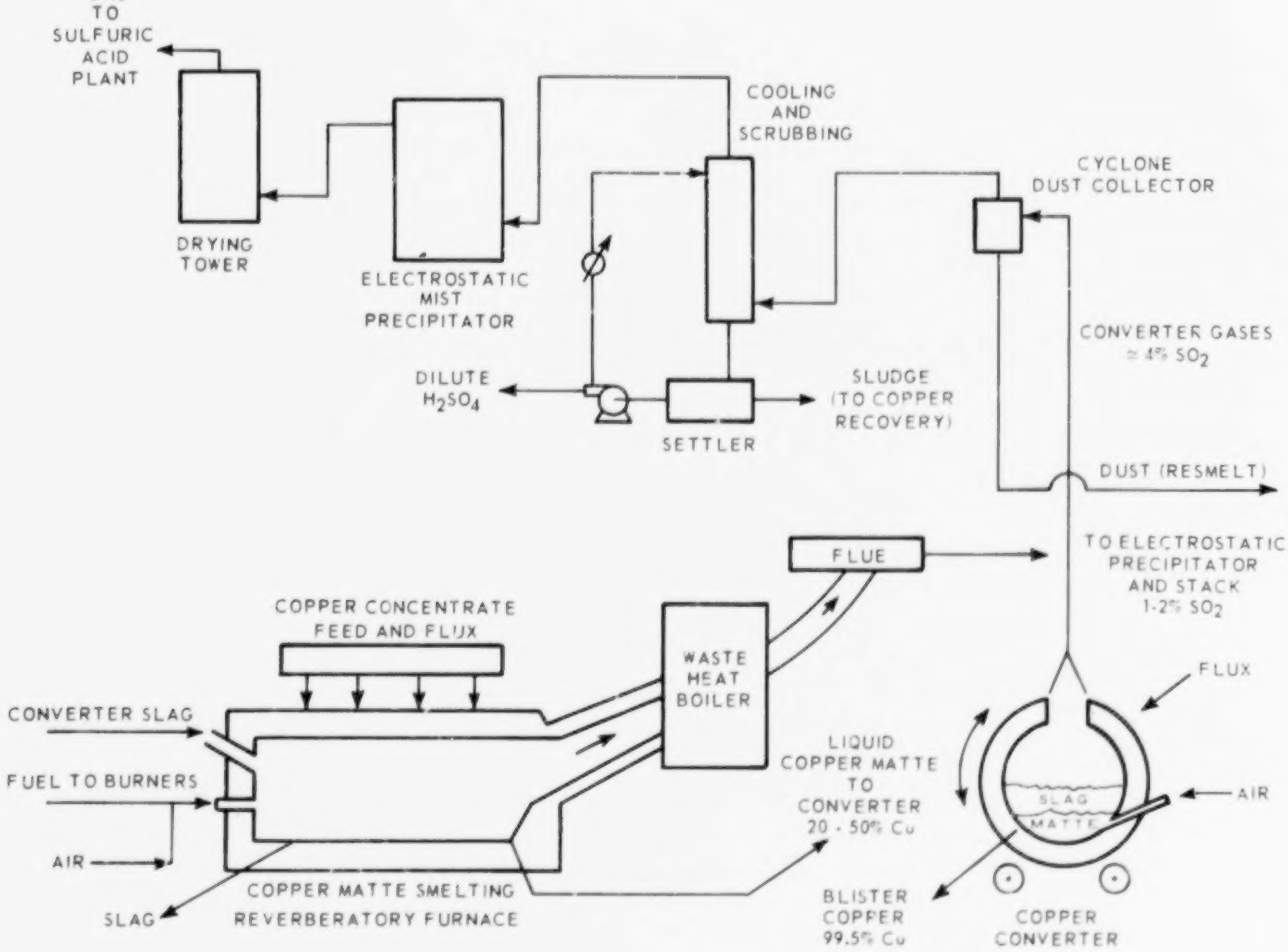
GAS TO SULFURIC ACID PLANT
DRYING TOWER
ELECTROSTATIC MIST PRECIPITATOR
COOLING AND SCRUBBING
CYCLONE DUST COLLECTOR
CONVERTER GASES ≈ 4% SO2
DILUTE H2SO4
SETTLER
SLUDGE (TO COPPER RECOVERY)
DUST (RESMELT)
FLUE
TO ELECTROSTATIC PRECIPITATOR AND STACK 1-2% SO2
COPPER CONCENTRATE FEED AND FLUX
WASTE HEAT BOILER
FLUX
CONVERTER SLAG
FUEL TO BURNERS
AIR
LIQUID COPPER MATTE TO CONVERTER 20 - 50% Cu
SLAG
MATTE
AIR
SLAG
COPPER MATTE SMELTING REVERBERATORY FURNACE
BLISTER COPPER 99.5% Cu
COPPER CONVERTER

Figure 5-1. Copper smelting with sulfur oxides recovery system.

blows with interspersed additions and adjustments. The first and second blows are for the purpose of slag formation and elimination of iron; the final blow completes the reduction of copper to an impure blister copper, which is refined elsewhere. Converter gases contain up to 6 percent SO_2, and are often fed to contact sulfuric acid plants.[3] Sulfuric-acid-plant feeds from nonmetallurgical sources normally range from 7 to 14 percent SO_2.[4] The metallurgical gases from smelters are more costly to treat because of the dilute nature of the gas stream and the presence of such impurities as dust and acid mist. These impurities must be removed with electrostatic precipitators, cyclones, or scrubbers before the gas enters a contact sulfuric acid plant. Each acid plant must be designed for the particular smelter-gas feed used. Because of the dilute nature of smelter-plant feed gases, 80 percent removal of SO_2 is considered a reasonable rate of recovery;[4] therefore, exit concentrations may still be as high as 0.8 percent, or 8000 ppm. More than 90 percent recovery of SO_2 and exit concentrations as low as 3000 ppm are obtained in some cases.

Reverberatory smelting usually dilutes the SO_2 in the gas stream so much that economic recovery as sulfuric acid is not feasible. Flash smelting processes would avoid such dilution and allow a high degree of sulfur recovery.[5] There are three fundamental pyrometallurgical copper operations: roasting, smelting, and converting. Flash smelting is a combination of roasting and smelting. Ore concentrate and preheated air are mixed and burned by being blown into the top of a vertical cylindrical furnace—the flash smelting furnace. Beneath this furnace is a settler, which is similar to a reverberatory furnace and is well insulated to retain matte in a molten condition. Combustion gas and roast blow down into the smelter from the flash furnace. The gas stream turns 90 degrees, and the roast falls into the molten pool of copper matte. The hot gases traverse the settler, move along the surface of the matte, and then are cooled from about 2300° to 1600°F in a waste heat boiler.[5] The gases are then further cooled by heat exchange against incoming smelting air and sent to a sulfuric acid plant. This process saves fuel and operates continuously. An SO_2 feed of constant concentration as high as 12 to 14 percent SO_2 can be sent to the sulfuric acid plant.

Flash smelting is possible when there is a substantial amount of sulfur in the concentrate above that actually required to form the copper matte.

Smelting with oxygen-enriched air is now practical because of the availability of bulk oxygen at reasonable prices.[6] This process reduces the amount of nitrogen involved in smelting, but has little effect on SO_2 emissions because it is used only in converting or flash smelting, both of which already produce relatively concentrated SO_2 gas streams. Oxygen-enriched air is not used in the reverberatory furnace, which produces dilute SO_2 gas and is the major source of SO_2 emissions from copper smelters.

The range of SO_2 emissions from individual smelters in the United States during 1968 was 11,000 to 536,000 tons per year.[7] The smaller amounts were emitted from smelters handling weathered copper ores (such as basic copper carbonates) or native copper; the larger amounts were caused by roasting ores high in sulfides or pyrites.

5.1.3 Lead Smelter Emissions Control

The most important ore of lead is galena (PbS). The lead ore concentrate is converted to oxide before reduction to metal. This is commonly done by sintering, wherein the following reaction takes place:

$$2\ PbS + 3\ O_2\ (air) \longrightarrow 2\ PbO + 2\ SO_2$$

Lead concentrates and lead-bearing residues and fluxes are spread over a continuous belt of grated pallets and ignited as the mass moves over a windbox. Oxidation of the sulfide furnishes the required roasting heat. Most of the sulfur is removed. The thickness and composition of the charge must be controlled so that it can be handled properly by the machine and will produce a roast with the required physical characteristics. The oxide is reduced to crude lead in a blast furnace, to which the sinter, together with coke, is charged. The crude lead from this furnace requires extensive further refining and silver, bismuth, and antimony are often important by-products.

Sintering steps produce appreciable sulfur oxide. The air aspirated through the burning bed of galena concentrate has an exit SO_2 content in the range of 1.5 to 5 percent by volume.[7] These gases can be fed to a contact sulfuric acid plant, after preliminary removal of dust and mists. If the SO_2 feed concentration is too low, it can be raised by burning pyrites or sulfur.

Emissions from individual lead smelters in the United States during 1968 ranged from 2000 to 82,000 tons of SO_2 per year.[7] No control cost data were found in the published literature.

5.1.4 Zinc Smelter Emissions Control

The metallurgy of zinc is unique among tonnage metals in that the boiling point of zinc (907°C) is lower than the temperature of reduction to metal (1100° to 1200°C).[10] The product of the reduction is a metal vapor.

Zinc occurs in the United States mainly as sulfide ores, the most common one being sphalerite (ZnS). This ore must be roasted and converted to an oxide before reduction to metallic zinc.

$$ZnS + 3/2\ O_2(air) \longrightarrow ZnO + SO_2$$

The roasted and/or sintered charge is reduced with coke to zinc metal. The metal is then purified in a high-temperature distilling tower. In this way, cadmium with its lower boiling point, lead with its higher boiling point, and other impurities are removed from the zinc. The reduction of sinter to metal can be done in several ways, but little if any SO_2 is emitted in the reducing step. Electrolysis is an alternative to distillation for purifying zinc.

Roasting is done in various furnaces, including: multiple-hearth (Herreshoff) furnaces, fluid-bed roasters, flash roasters, and sintering furnaces. Typical analyses of gases leaving these roasters are shown in Table 5-2.[9] The SO_2 concentrations shown in the table are suitable for feed to a sulfuric acid plant. Pretreatment equipment to remove dust and metals is required.

A large new plant, which processes zinc ore concentrates containing about 32 percent sulfur, has recently begun operation.[10] Fluid-bed roasters operate autogenously at about 1900°F, generating a roaster gas containing 10 to 12 percent SO_2. The associated sulfuric acid plant can operate on this gas, on sulfur burner gas, or with combinations of these gases. Dust the roaster gas amounts to about 15 percent of the roaster feed and is removed by a cyclone, an electrostatic precipitator, and a scrubbing tower, followed by an electrostatic mist precipitator and a sulfuric acid drying tower. All this equipment is required to make the roaster gas suitable for feeding to the contact sulfuric acid plant. The dust removed from the roaster gas is returned to the zinc-ore-concentrate pelletizing system. The gaseous effluent from the sulfuric acid plant contains less than 2000 parts per million of SO_2 by volume.

Table 5-2. SULFUR DIOXIDE CONCENTRATIONS FROM ZINC ROASTERS

Roasting furnace	SO_2 in exit gas, volume percent
Multiple hearth	5–7
Fluid bed	6–12
Flash	6–8
Sintering	4.5–7

The capital cost of a 200-ton-per-day sulfuric acid plant handling gases from a zinc roaster plant,[11] adjusted to 1968 costs, is over \$1.8 million. If the SO_2 is assigned no value, the total cost of the acid would be about \$10.70 per ton. A comparison of total sulfuric acid costs from this zinc roaster gas plant and a 200-ton-per-day, sulfur-burning acid plant[11] suggests an advantage of over \$10 per ton for acid from the roaster gas plant, based on 1968 sulfur price levels.

These rough estimates are based on costs given in the reference and cannot be used to generalize.

5.2 PETROLEUM REFINERIES

5.2.1 Introduction

As of January 1968, there were 269 operating petroleum refineries in the United States with capacities ranging from a few thousand to 430,000 barrels per day.[12] In some urban areas of the United States there are several refineries with a combined crude processing rate of over 800,000 barrels per day. Refinery processing during 1966 resulted in SO_2 emissions estmiated at 1,583,000 tons, or approximately 5.5 percent of total SO_2 emissions in the United States.[1]

In some areas, considerable effort has been made to control SO_2 emissions. In many insances, modern refinery processes have, of necessity, integrated air pollution control into their operations.

Sulfur removal from some refinery streams is a part of refining. It would be desirable to remove all sulfur compounds before any processing of the crude begins, but since this is impractical, sulfur is removed in subsequent steps throughout refinery processing. There are several reasons, other than air pollution control, for removing sulfur from intermediate fractions and products of crude oil. Sulfur removal reduces corrosion, odor, number of breakdowns, catalyst poisoning, and gum formation and improves octane rating, color, and lube oil life.[14]

5.2.2 Petroleum Refining Processes

Most oil refinery processing units are made up of at least five main types of equipment: heaters, reactors, vessels, heat exchangers, and pumps. The arrangement, type, and quantity of this equipment are set up to fit the particular function desired, such as separation, conversion, treating, or blending.[15] Separation is accomplished by distillation; conversion by cracking and reforming; and treating by various methods, the most popular of which is hydrogen treating.

5.2.2.1 Distillation—Separation of a mixture of light and heavy hydrocarbons into various fractions is usually done by distillation. The first step in refining crude oil to gasoline is atmospheric distillation, whereby crude oil is separated into gas, naphtha, diesel oil, gas oil, and topped crude. Further refining of fractions will again entail the use of distillation equipment. Almost every major processing unit in the refinery has, as a part of its unit, a distillation section.

5.2.2.2 Cracking or Pyrolysis—Conversion, by cracking large hydrocarbon molecules into smaller ones, is done by the application of heat and/or catalysis. At the same time some of the cracked molecules recombine (polymerize) to form larger molecules; thus, a synthetic crude that can be separated into gaseous hydrocarbons, gasoline, gas oil, and fuel is formed. A large selection of materials ranging from ethane to heavy crude residiums can be cracked.

The two kinds of cracking are thermal and catalytic. Thermal cracking, using high temperature and pressure, is generally applied to the cracking of distillates heavier than gasoline. Delayed coking, fluid coking, and visbreaking are examples of thermal cracking processes. Catalytic cracking uses high temperatures and chemical catalysts to crack the molecules into synthetic crude. The result is a faster and more complete breakdown of heavy feed stock than is accomplished by thermal cracking. There are only two methods of catalytic cracking in general use: the more popular, fluidized-bed method typified by a Fluid Catalytic Cracking unit (F.C.C.) and the less commonly used moving-bed method, as used by Thermofor Catalytic Cracking units (T.C.C.).

5.2.2.3 Hydrocracking—The hydrocracker uses a fixed-bed catalytic reactor, wherein cracking occurs in the presence of hydrogen, under substantial pressure. The principal functions of the hydrogen are to suppress the formation of heavy residual material and to increase the yield of gasoline by reacting with the cracked products.[16] High-molecular-weight, sulfur-bearing hydorcarbons are also cracked, and the sulfur combines with the hydrogen to form hydrogen sulfide (H_2S). Therefore, waste gas from the hydrocracker contains large amounts of H_2S, which can be processed for removal of sulfur.

5.2.2.4 Reforming—Catalytic reforming units are used to produce higher octane gasoline by rearranging the molecular structure of straight run and light naphtha feedstock. The reaction is achieved in a fixed-bed catalytic reactor by reactions of the feedstock in the presence of hydrogen over a platinum catalyst. Hydrogen, produced as a by-product, is partly recycled to the reactor, with the excess used in hydrogen treating units for sulfur removal and product improvement.

5.2.2.5 Polymerization and Alkylation—Gasoline is produced in polymerization and alkylation units by combining gaseous hydrocarbons. Gaseous olefins will combine to polymerize into high-octane gasoline. Alkylation combines olefins with isobutanes. These processes operate as closed systems and do not cause a significant air pollution problem under normal operating conditions.

5.2.2.6 Hydrogen Treating—The hydrogen treating process consists of bringing oil charge stock and hydrogen into a fixed-bed, catalytic reactor at an elevated temperature and pressure. Under the influence of the catalyst, hydrogen reacts with sulfur, nitrogen, oxygen, and olefinic hydrocarbons to form removable H_2S, ammonia, saturated hydrocarbons, and water.[16] In addition, metals are reduced to elemental form. Large quantities of hydrogen are required if any extensive use of hydrotreating and hydrocracking is done.

The process gas from this unit is rich in hydrogen, hydrocarbons, and H_2S. Hydrogen sulfide can be extracted from this stream and converted to elemental sulfur or sulfuric acid.

5.2.2.7 Hydrogen Production—Hydrogen is now of extreme importance in refining. For example, Kuwait National Petroleum is building what is considered the first "all-hydrogen" refinery in the world.[17] It includes residuum hydrogenation and hydrotreating. Table 5–3 shows the components of this 95,000-barrel-per-day refinery.

The hydrogen manufactured by the hydrogen plant, plus whatever byproduct hydrogen is produced by the catalytic reformer, is used in the two hydrocrackers, four desulfurizers, and the catalytic reformer, for the purpose of product upgrading and feedstock preparation. In doing this, large amounts of organic sulfur compounds are hydrogenated to H_2S and contained in the sour gas stream coming from these units. This H_2S is removed from the gas stream in an extraction system and then converted to elemental sulfur in the sulfur recovery facility. Therefore, the importance of the extensive use of hydrogen is not only reflected in product upgrading and feedstock preparation but also in the production of a large amount of recovered sulfur from processing a sour crude.

Table 5–3. CAPACITY OF THE COMPONENTS OF A 95,000-BARREL-PER-DAY REFINERY

Component	Capacity
Crude unit	95,000 bbl/day
Catalytic reformer	15,820 bbl/day
H-Oil unit (hydrocracker)	23,460 bbl/day
Isomax unit (hydrocracker)	14,400 bbl/day
Four unifiners (desulfurizers)	80,000 bbl/day
Hydrogen plant	140 million cf/day
Sulfur recovery unit	570 lt/day

5.2.3 Sulfur Dioxide Emissions

If controls are not applied, emissions of SO_2 from refinery operations can be appreciable. For example, it has been shown that if all H_2S produced in Los Angeles County from processing approximately 650,000 barrels of crude per day were burned instead of being controlled, 800 tons of SO_2 would be discharged into the atmosphere per day. Furthermore, 200 to 300 tons of SO_2 would be emitted per day by burning acid sludge that comes from sulfuric acid treating.

5.2.3.1 Heaters and Boilers—In many instances refinery SO_2 emissions come from burning organic sulfur compounds contained in the fuel used as energy sources for process heaters and refinery boilers. Almost every major processing unit in an oil refinery includes one or more process heaters. Such fuels as refinery gas, natural gas, heavy residual fuel oil, and coke are used. Sulfur-dioxide flue-gas concentrations, ranging from 700 to 1000 parts per million, resulting from burning heavy residual fuel oil have been measured.[18] The SO_2 flue-gas concentration varies, depending mainly upon the sulfur content of the fuel and, to a lesser extent, the operating conditions.

5.2.3.2 Catalytic Regeneration—A catalyst, after extended use, loses some of its activity and requires regeneration. Regeneration is accomplished by applying a controlled volume of air to burn off coke deposits at a controlled temperature, which in turn creates an effluent gas containing dust, carbon monoxide, and SO_2.

Catalyst can be regenerated continuously as in the Fluid Catalytic Cracker (F.C.C.) or the Thermofor Catalytic Cracker (T.C.C.), where the catalyst is continuously removed from the reactor, generated in a large vessel, and recycled to the reactor. The F.C.C. regenerator is one of the larger single sources of SO_2 emissions in an oil refinery. Tests made in Los Angeles County on six F.C.C. units with a combined fresh feed rate of 156,000 barrels per day and nine T.C.C. units with a combined fresh feed rate of 69,000 barrels per day showed emissions of 42 tons per day and 2 tons per day, respectively. The SO_2 concentration of the F.C.C. flue gas ranged from 308 to 2190 parts per million.[15] The SO_2 concentration of the catalytic cracking unit regenerator flue gases can vary over wide limits, depending on the amount of sulfur in the feed stock and on operating conditions.

In a fixed-bed system, such as a reformer or hydrotreater, the reactor is periodically taken off stream to regenerate the catalyst. The SO_2 emission from regeneration of a fixed-bed catalyst is not significant.

5.2.3.3 Treating—The quantity of sulfur emitted from treating operations depends primarily on the methods used for handling spent acid and acid sludge, and on recovery or disposal of H_2S. Settling tank vents, surge tanks, water treatment units, waste-water drains, valves, and pump seals in the treatment area may be sources of trace quantities of malodorous substances such as H_2S and mercaptans.

Hydrogen treatment generates large quantities of H_2S. Unless available methods are used to remove the H_2S, it is used as part of the fuel feed to heaters or boilers, which results in the emission of large quantities of SO_2.

5.2.3.4 Acid Sludge Disposal—Sludge contains from 25 to 70 percent acid, the remaining portion being mostly heavy hydrocarbons, alkyl sulfides, and thiophenes.[16] This sludge may be disposed of by burning it as a fuel, and thus creating large quantities of SO_2 emissions. There are other methods of disposal, such as making by-products, processing for acid recovery, and dumping in the ground or at sea.

5.2.3.5 Flares—Waste gas produced by a refinery can be handled by one or more flare systems. The sulfur content of the waste gas to each flare system depends on its source, since it can come from one or more refinery operating units. The combustible composition of waste gas and the temperature in the combustion zone determine whether sulfur compounds are sufficiently burned to SO_2 or released in a more odoriferous form. Sulfur dioxide and other injurious substances in hydrocarbon waste gases should be removed by some type of absorption system before going to a flare. Examples of flare preabsorption systems would be SO_2 removal from an Edeleanu treating unit, HF from an alkylation unit, and HC from an isomerization unit.

5.2.3.6 Vacuum Jet Exhausters—Vacuum jets are used to operate a process vessel at less than atmospheric pressure, to remove hydrocarbon gases from equipment during shutdowns, and to evacuate the gases from fixed-bed reactors before regeneration. The steam jet exhauster on the crude-unit vacuum tower, for example, continuously draws a vacuum on the tower in which the temperature of the heavy residuum may be high enough to cause some cracking of the organic sulfur constituents into H_2S. The H_2S, in turn, is exhausted by the steam jet exhauster and discharged with the uncondensed gases. The volume of gas is not great, but it may contain as much as 25 percent H_2S, by volume.

5.2.3.7 Air Blowing of Asphalt — Asphalt from the crude unit can be made into roofing asphalt by subjecting it to air blowing at elevated temperatures. Air is passed through the charge in the steam-blanketed still at an approximate rate of 40 cubic feet per minute per ton of charge until the desired hardness is achieved.[17] In addition to sulfur compounds, the effluent gases contain hydrocarbons and aerosols.

5.2.3.8 Miscellaneous Sources—There are several other refinery sources of SO_2 emissions, such as decoking, air blowing for brightening petroleum distillates, and waste-water treatment.

5.2.4 Control of Sulfur Oxides

Table 5–4 is a compilation of typical refinery sources of sulfur compound emissions.

Table 5-4. SOURCES OF SULFUROUS EMISSIONS AND CONTROL METHODS

Source containing sulfurous compounds			Usual control		Recommended control method	
Unit	Make gas	Waste gas	Small plant	Large plant	Small plant	Large plant
Distillation:						
Crude topping	Fractionating column overhead accumulator		Refinery fuel system or incinerated	Saturated gas recovery plant	Caustic scrubbed before disposal	Amine scrubbed in saturated gas recovery plant
Vacuum		Vacuum exhausters	Incinerated	Incinerated	Scrubbed and incinerated	Scrubbed and incinerated
Thermal cracking:						
Delayed coker	Main fractionator overhead accumulator			Amine scrubbed		Amine scrubbed
Delayed coker		Coke drum blowdown		Flared		Absorption unit with tail gas to flare
Catalytic cracking:						
FCC unit		Regenerator		CO boiler and electrostatic precipitator.[a]		CO boiler and electrostatic precipitator, no economical method now available for sulfur removal
FCC unit	Reactor			Cyclone [b]		Amine scrubbed
TCC unit		Regenerator		Cyclone [b]		Cyclone and scrubber
Air blown asphalt		Asphalt still	Water scrubbed with off gas to atmosphere	Water or gas oil scrubbed with off gas to atmosphere	Water or gas oil scrubbed with off gas to incinerator	Water or gas oil scrubbed with off gas to incinerator
Gas plant		Compressor failure		Flare		Flare
Reformer		Catalyst regeneration		Regeneration gas to atmosphere		Scrubbed and then to atmosphere
Hydrogen treating		Catalyst regeneration	Diluted in stack gas	Diluted in stack gas	Scrubbed and then to atmosphere	Scrubbed and then to atmosphere
Hydrogen treating	H_2S from separator		Flare or boiler firebox	Flare, boiler firebox or sulfur recovery	Sulfur recovery	Sulfur recovery
Miscellaneous:						
Unit relief valves	Reactors, columns, etc.		Flare	Vapor recovery with overload to flare	Vapor recovery with overload to flare	Vapor recovery with overload to flare
Unit relief valves		H_2S absorption unit	Flare	Flare	Flare	Flare

Unit relief valves	SO_2 extraction unit	Atmosphere	Atmosphere	Scrubbed with caustic solution	Scrubbed with caustic solution
Sour water oxidizer	Separator [a]	Off gas to atmosphere	Off gas to atmosphere	Off gas to incinerator	Off gas to incinerator
Storage tanks	Hydrocarbon vapors with high concentration of H_2S	Fixed roofs	Floating roofs, vapor balance	Floating roof, vapor balance, vapor recovery	Floating roof, vapor balance, vapor recovery
Heaters, boilers				Use low-sulfur fuel or remove SO_2 from stack	Use low-sulfur fuel or remove SO_2 from stack
Sulfur plant	Sulfur plant tail gas	Incinerated	Incinerated	Incinerated	Incinerated

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[a] Controls carbon monoxide, hydrocarbons, and particulates only.

[b] Controls particulates only.

The specific unit, process gas source, waste gas source, usual method of disposal, and recommended method of control are shown. Process gas is defined as that gas produced in a processing unit. It comes from such units as catalytic cracking units and reformers. Waste gas is the gas emitted from processing units that cannot be used further. For instance, crude vacuum tower exhaust gas, which has an insufficient heating value to be used as a fuel, and emergency relief gas, which is beyond the normal capacity of vapor recovery systems, are waste gases.

5.2.4.1 Heaters and Boilers—The concentration of SO_2 emitted from heaters and boilers can be lowered by burning low-sulfur fuel oil, low-sulfur process gas, or natural gas.

Since the demand is now becoming greater for low-sulfur fuel oil, U.S. refineries may have difficulty selling high-sulfur fuel oil. Consequently, refineries that make high-sulfur fuel oil in areas of the United States where there are no restrictions limiting the amount of sulfur in the fuel oil will probably use it in their process heaters and boilers, as a supplement to burning process gas and natural gas. Some refineries, particularly on the West Coast, make no heavy fuel oils. The general trend in refinery processing in this country is toward more conversion of feed stock to distillate oils.

5.2.4.2 Catalytic Regeneration Gases—The removal of SO_2 from the regeneration gases of F.C.C. and T.C.C. units is not practiced at this time; however, current studies being made on systems for the removal of SO_2 from combustion gases in power plants may find that, in the future, these systems can be used on F.C.C. units because the SO_2 concentrations in the F.C.C. effluent gas are comparable to those of some power plants. An alternative method would be to desulfurize the feedstock.

The removal of SO_2 from the regeneration gases of a fixed-bed catalytic reactor can be accomplished by caustic scrubbing. Since the volume of gas during regeneration is limited, and regeneration is required infrequently (in some instances once and other instances a few times per year, depending on the type of unit and operations performed), the cost of sulfur removal would not be high.

5.2.4.3 Treating—Table 5–5 shows 12 of the many methods of desulfurizing petroleum products and feedstocks.[14] Method 1 shows one way of removing H_2S; however, in order to prevent sulfurous emissions when the gas is later burned, the H_2S in the stabilizer off-gas should be separated from the gaseous hydrocarbon. This can be done by method 8, provided the elemental sulfur recovery is desired, or by a caustic-wash scrubber. Similarly, H_2S should be removed from the stabilizer off-gas resulting from the use of the hot clay treating process (method 10). Sulfuric acid treatment (method 2) removes most sulfur compounds, plus some hydrocarbons, to form an acid sludge. This method is gradually being replaced by other methods. An acid recovery system, replacing the burning of acid sludge, is one way to alleviate the problem of large quantities of SO_2 emissions. Sweetening processes used for light distillates (methods 3, 4, and 5), remove very little if any sulfur or sulfurous compounds from the liquid product, but will convert them to a less deleterious form. Caustic scrubbing, used alone (method 7) or with promoters (method 8), removes mercaptans by chemical reaction. Some of these caustic treating processes are regenerative. Spent caustic is sometimes sold to chemical plants for conversion to chemicals. Because of excessive costs and disposal problems, the use of caustic has been largely replaced by other methods, except in the removal of trace amounts of acid gases. Hydrogen sulfide generated in hydrogen treating operations (method 11) should be removed from the process gas by amine scrubbing or some similar operations. The cleaned gas can then be used for refinery fuel and the removed H_2S can be further processed into elemental sulfur or sulfuric acid. If the quantity of H_2S is too small to economically justify recovery, it should be caustic scrubbed, with the residual gas going to an elevated flare or boiler firebox. Considering the added cost of caustic scrubbing, sulfur recovery seems to be the better choice.

5.2.4.4 Air Blowing of Asphalt—The effluent gas stream from an asphalt still, containing sulfur compounds, hydrocarbons, odors, and

Table 5-5. DESULFURIZATION METHODS AND THEIR EFFECTS ON REMOVAL OF VARIOUS SULFUR COMPOUNDS[a]

No.	Desulfurization method	Elemental sulfur	Hydrogen sulfide	Mercaptans	Sulfides	Thiophene	Disulfide	Polysulfide
1.	Fractionation and stabilization	Removed by fractionation to bottoms	Removed by stabilization	—	—	Largest percent fractionated to bottoms	Largest percent fractionated to bottoms	Largest percent fractionated to bottoms
2.	Sulfuric acid treatment:							
	Fuming acid	Prior removal (dissolves if not removed)	Prior removal	Converted to disulfides	Complete removal	Complete removal	Complete removal	Complete removal
3.	Concentrated acid	Prior removal	Prior removal	Converted to disulfides	Partial removal	Partial removal	Partial removal	Partial removal
4.	Doctor treatment	Reacted with mercaptans to form disulfides	Prior removal	Converted to disulfides	No effect	No effect	No effect	May be formed thru improper doctor treatment
5.	Alkaline hypochlorite	No effect	Prior removal or oxidized to free sulfur	Oxidized to disulfides	May be oxidized	No effect	Partially oxidized to sulfonics and sulfonic acid	Same as effect on disulfides
6.	Copper treatment	Prior removal	Prior removal	Converted to disulfides	No effect	No effect	No effect	No effect
7.	Caustic wash	Removes [a]	Removes	Largely removed [b]	No effect	No effect	No effect	Little if any effect
8.	Mercapsol, Unisol, and Pannin Solutizer	Prior removal	Prior removal	Removes	No effect	No effect	No effect	No effect
9.	Ethanolamine and phosphate	No effect	Removes	No effect	No effect	—	—	—
10.	Hot clay treatment	Forms H_2S or other compound	No effect	Decomposed	Largely converted to H_2S	Little effect	Largely decomposed	Decomposed
11.	Cat. desulf. with outside hydrogen	Combines with H_2	No effect	Decomposed H_2S formed	Decomposed H_2S formed	Decomposed H_2S formed	Decomposed H_2S formed	Decomposed H_2S formed
12.	Sodium treatment	Removes	Removes	Removes	Removes at elevated temperature	Removes at elevated temperature	Removes	Removes

[a] Alkaline polysulfide wash removes free sulphur when properly controlled.

[b] Depends upon number of stages and boiling range of mercaptans.

aerosols, is objectionable if discharged directly into the atmosphere. The effluent stream may first be water scrubbed to remove some of the hydrocarbons and then incinerated in a boiler, a heater firebox, or a specially built incinerator. The combustion of sulfur-bearing gases yields SO_2.

5.2.4.5 Sulfur Recovery Facilities—Sulfur plants and sulfuric acid plants associated with oil refineries are of considerable importance in the control of SO_2 emissions. Modern dry refinery methods have greatly increased the removal of sulfur from crude oil derivatives. Up to 85 percent of the sulfur in crude oil can be converted to H_2S by using modern refinery methods.

For example, in a 100,000-barrel-per-day refinery processing a 31.2° API* crude oil with 2.5 percent sulfur content, the total amount of sulfur in the crude used each day is approximately 330 long tons. The use of modern processes in such a refinery could result in the production of a fuel oil containing 1.5 percent sulfur, and the recovery of 250 long tons of sulfur per day. If a fuel oil of 0.5 percent sulfur were produced, the potential sulfur production would be 285 long tons per day.[19]

It can be seen by referring to Table 5–5 that only a few of the methods will remove H_2S. However, if sulfur is to be made from H_2S, a regenerative type of H_2S removal process should first be used to remove the H_2S from the sour gas stream. One of these, as shown in the table, is ethanolamine absorption of H_2S. In addition to ethanolamine, there are several other regenerative absorbents in use. The criteria for the selection of the H_2S removal process and the absorbent are: (1) type of impurities in the gas stream such as H_2S, CO_2, RSH, COS, and CS_2, (2) impurity concentration, (3) amount of impurity removal desired, (4) acid-gas selectivity required, (5) feed gas volume, and (6) temperature-pressure of feed gas.[23]

In addition to the ethanolamine process, the following processes can remove H_2S from gaseous hydrocarbons by a liquid absorption/desorption method: (1) hot potassium carbonate, (2) water washing, (3) seaboard and vacuum carbonate process, (4) tripotassium phosphate, (5) sodium phenolate, (6) Giammarco-Vetrocoke process, (7) Catacarb process, (8) Shell Sulfinol process, (9) Fluor solvent process, and (10) vacuum carbonate.[20]

The use of ethanolamines is an established method for removing H_2S. Figure 5–2 is a flow chart for such a process. Either monoethanolamine or diethanolamine in aqueous solution can be used as the absorbent. Hydrogen sulfide reacts with the amine to form a compound that can be decomposed by heat.

The hydrocarbon gas (sour gas), rich in H_2S, enters the bottom of the absorber. The lean amine solution contacts the gas countercurrently and absorbs the H_2S. The desulfurized gas leaves the top of the column, and the rich amine solution leaves the bottom of the column and goes through the heat exchanger into the regenerator column. In the regenerator, H_2S is stripped from the rich amine solution by heat and passes out of the tower as a concentrated acid gas. The acid gas from the regenerator column is cooled and then sent to the sulfur plant. The lean amine solution leaving the regenerator reboiler is cooled and sent to the amine storage tank, from which it will be pumped back to the absorber to repeat the cycle.

Upset conditions of this unit could result in releases of hydrocarbons and H_2S. The usual procedure in this case is to connect relief valves to a flare system, allowing any release of hydrocarbons and H_2S to be incinerated by the flare. Also, during malfunction of the sulfur plant the acid gas flow can be diverted to the flare system. A well designed and properly maintained sulfur plant will help to prevent frequent emergency releases of gas to the flare.

Hydrogen sulfide removal systems are most often located at several unit areas within a refinery. Sometimes the regeneration part of the facility is located in a chemical company near the refinery. The chemical company pipes lean amine solution to one or more refinery units where H_2S is removed, and the rich amine is piped back to the chemical company. Acid gas is used by the chemical company to manufacture sulfur.

The Claus process (developed about 1890) is the most widely used method of producing sulfur from refinery H_2S.[21] The modified Claus process (developed about 1937) is based on producing elemental sulfur by first converting one-third of the H_2S feed by precise combustion with air to achieve the following reaction:

---

*°API—specific gravity scale established by the American Petroleum Institute

$$2\ H_2S + 3\ O_2 \longrightarrow 2\ SO_2 + 2\ H_2O$$

The above products of combustion are then further reacted with the two-thirds unreacted H_2S feed in the presence of a suitable catalyst to form sulfur vapor:

$$2\ H_2S + SO_2 \xrightarrow{\text{catalyst}} aS_2 + bS_6 + cS_8 + 2\ H_2O$$

The letters a, b, and c represent the number of mols of the various possible molecular forms of sulfur vapor.[21]

Sulfur vapor is formed in both the combustion reaction and in the catalytic conversion reaction; however, regardless of how much sulfur is formed in the combustion reaction, it can be shown stoichiometrically that the required amount of oxygen is that quantity which will react with one-third of the H_2S in the acid gas feed and convert it to SO_2.[22] After each reaction, the sulfur vapor is condensed to liquid sulfur and allowed to drain to sulfur storage.

Figure 5–3 shows a typical process flow chart for one type of modified Claus sulfur plant. The total acid gas stream enters a waste heat and reaction furnace where one-third of the acid gas is burned with a controlled amount of air. The exotherimc reaction in the waste heat and reaction furnace is used to produce steam. Sulfur vapor formed in the primary reaction is condensed in the No. 1 condenser and drained to liquid sulfur storage. The uncondensed gases leaving the condenser go to the No. 1 converter where, with the use of a catalyst at a controlled temperature, some of the H_2S is converted to more sulfur vapor. The temperature of the converter inlet gas stream is elevated to the optimum conversion temperature (475°F) by combining with a slip stream of about 900°F from the hot gas stream of the reaction furnace. The sulfur vapor, formed by the No. 1 converter, is condensed by the No. 2 condenser. Uncondensed vapors, before entering the No. 2 converter, mix with a hot-gas slip

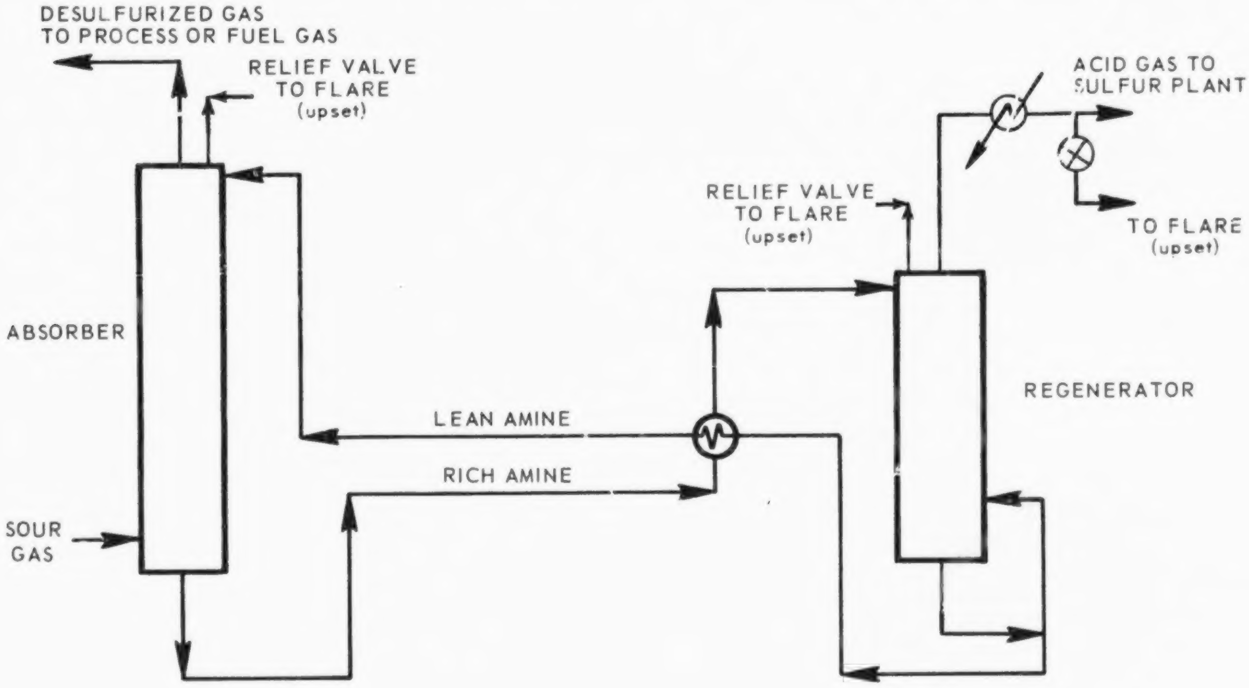
DESULFURIZED GAS TO PROCESS OR FUEL GAS
RELIEF VALVE TO FLARE (upset)
ABSORBER
SOUR GAS
LEAN AMINE
RICH AMINE
RELIEF VALVE TO FLARE (upset)
ACID GAS TO SULFUR PLANT
TO FLARE (upset)
REGENERATOR

Figure 5-2. Flow chart for H_2S removal by amine solutions.

stream from the reaction furnace. Converter No. 2 vapor passes to No. 3 condenser and then enters a coalescer for the removal of any entrained sulfur droplets. From the coalescer the gases go to an incinerator where the residual tail gas, containing sulfur compounds, is converted to SO_2 and diluted with air before the effluent gases are discharged into the atmosphere.

Several types of catalysts have been used, but bauxite appears to be the most desirable because of low cost, durability, and high activity.[21] The catalyst-bed thickness is limited since the reaction is exothermic and low temperatures favor the conversion. It has been shown that a one-stage plant (one converter) with an excessively thick catalyst bed is not feasible for quaranteed high conversion efficiencies.[23] A one-stage converter plant can operate with efficiencies up to 85 percent. With two stages, efficiencies have been reported as high as 95 percent. From an air pollution point of view, it is imperative that all plants be designed with at least two and possibly three catalytic converter stages.

For a minimum discharge of sulfur compounds to the atmosphere, and a maximum conversion to sulfur, the initial ratio of H_2S to SO_2 should be maintained at the stoichiometric ratio of 2 mols of H_2S to 1 mol of SO_2. To maintain this ratio, the correct amount of air must be metered into the reaction furnace. Figure 5–4 shows what happens when the correct amount of air is not supplied.[23] For example, if the initial ratio of H_2S to SO_2 is not at the desired ratio of 2 and is instead 1.3, then the initial ratio will become lower from point to point in the plant as the conversion increases until it theoretically approaches zero at 84.8 percent maximum conversion.[22]

Recently, there has been introduced on the market a costly and sophisticated instrumentation system that will automatically adjust the flow of air to maintain optimum operating conditions. For larger sulfur plants, it has been stated that the amount of additional sulfur manufactured by the use of this instrumentation will result in a payoff of the instrumentation in a few years.[24]

A sulfur plant should be designed to prevent as many operating difficulties and shutdowns as possible, and standby equipment should be installed. For example, one refinery on the East Coast built a sulfur plant with two reaction furnaces to provide for a range of practical operating flexibility. This arrangement also allows periodic servicing of one reaction furnace while the other unit remains in operation.

5.2.5 Sulfur Plant Costs

Large sulfur plants operate more economi

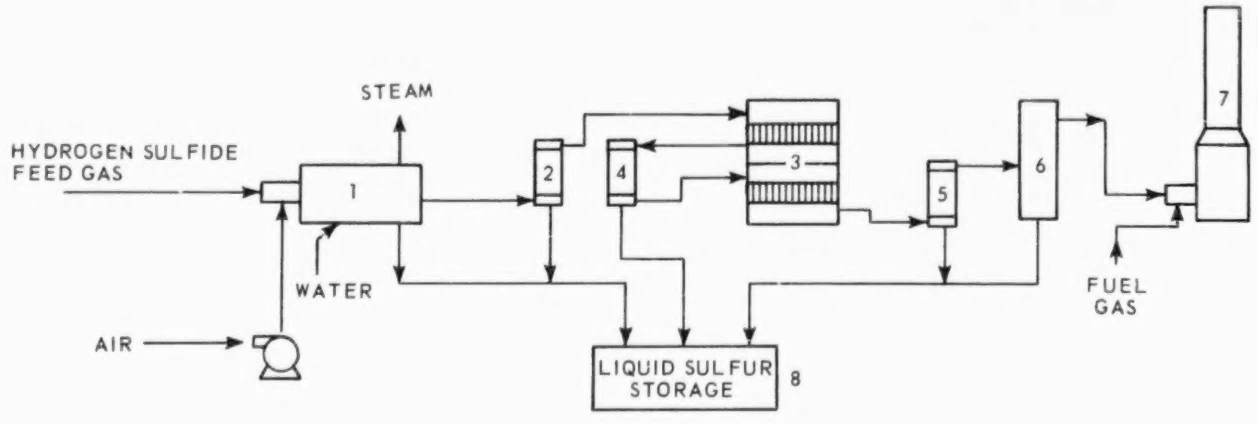

Figure 5-3. Sulfur recovery plant (flow chart).

cally than small ones. Table 5–6 shows that there is a large potential source of sulfur, either from desulfurizing the fuel oil or from converting it to distillate fuel oil. Table 5–7 shows new construction in the United States and other areas to recover this sulfur from oil refineries and natural gas producing areas.[25] Costs, as shown, do not indicate whether the H_2S removal facility is included with the sulfur recovery plant.

In the last 10 years, the recovery of sulfur in the United States has grown very rapidly and has reached 25 percent of the free-world production.

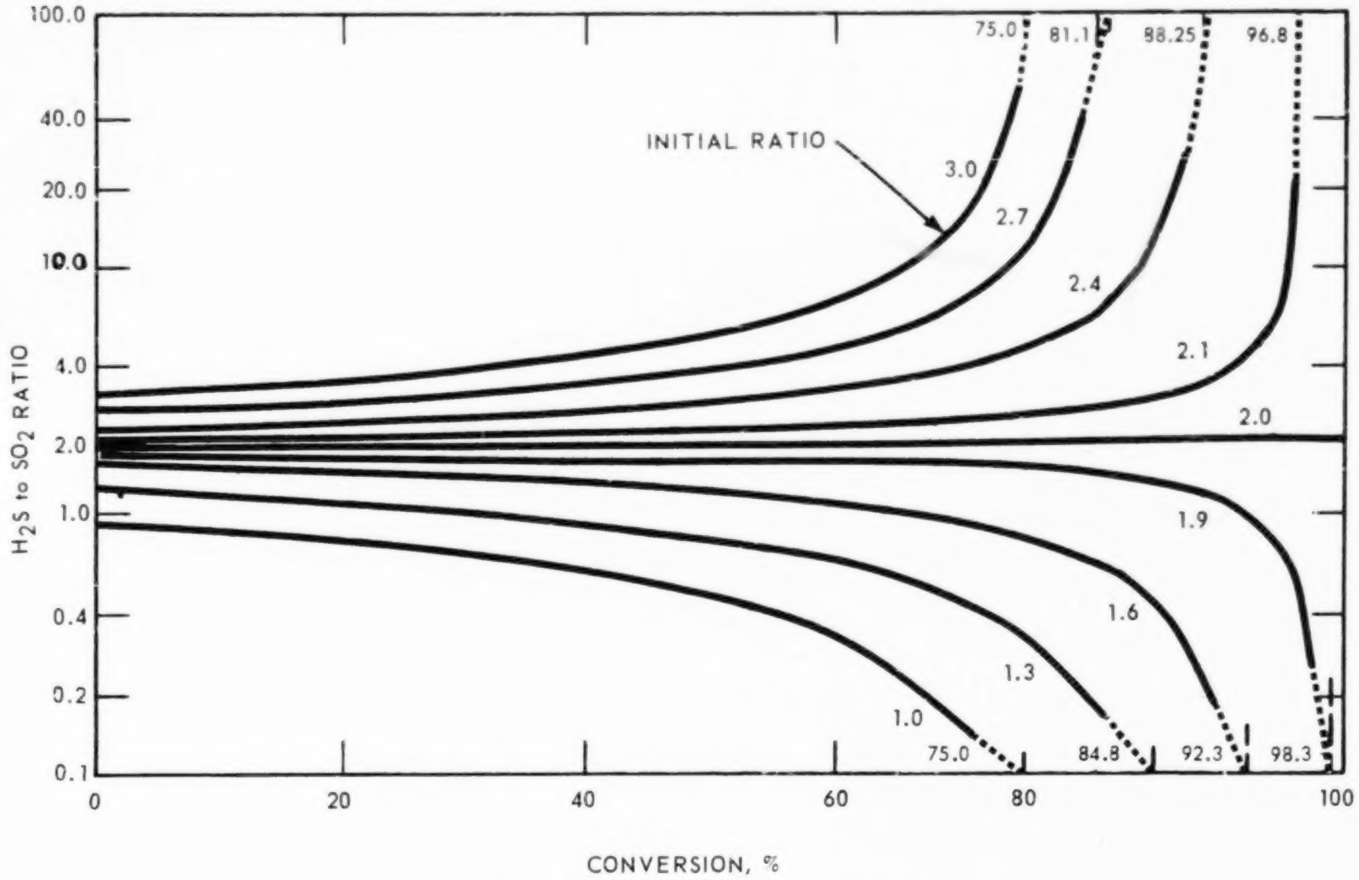

Figure 5-4. Variation of H_2S to SO_2 ratio with conversion and maximum theoretical conversion possible at specified ratio.

Table 5–6. DISPOSITION OF SULFUR IN NET PRODUCTS CONSUMED IN UNITED STATES—1962
[Excluding Rocky Mountain Region]

	Net product consumed, 1000 bbl	Sulfur content, percent	Sulfur, tons/day	Approximate percent total sulfur burned
Gasoline	4,166	0.043	228	5.0
Kerosene (including commercial jet)	439	0.079	49	1.2
Military jet fuel	291	0.067	27	0.6
Distillate fuel oil	1,909	0.213	599	13.2
Residual fuel oil	1,456	1.428	3,625	80.0
Asphalt	297			
All other	798			
Totals	9,356		4,528	100.0

Table 5-7. NEW SULFUR PLANTS COMPLETED OR UNDER CONSTRUCTION AS OF FEBRUARY, 1968[25]

Company	Plant site	Daily capacity, tons	Probable completion	Source	Cost dollars
UNITED STATES					
Ashland Oil and Refining	Buffalo, N.Y.	50	Early 1969		
	Canton, Ohio	50	Mid. 1969		
Cities Service	Myrtle Springs, Texas		Summer 1968		
	Van Zandt County, Texas	300	Sept. 1968	Natural gas	
	Roosevelt County, N.M.	30	Complete	Natural gas	
Continental Oil	Denver, Colo.	18	Complete		500,000 with amine unit
Farmers Union Central Exchange	Laurel, Mont.	28	Early 1969	Petroleum refining	1,000,000
Humble Oil and Refining	Linden, N.J.	270	Late 1968	Petroleum refining	1,500,000
	Benicia, Calif.	135	1968	Petroleum refining	
Marathon Oil	Detroit, Mich.	—	—	Petroleum refining	
	Iraan, Texas	11	Complete		
Northwestern Refining	St. Paul, Minn.	40	Complete	Petroleum refining	
Phillips Petroleum	Kansas City, Mo.	22	1968	Petroleum refining	
Powerine Oil	Santa Fe Springs, Calif.	—	1968	Petroleum refining	
Union Oil Co. of California	Lemont, Ill.	25	Early 1970		
CANADA					
Hudson's Bay Oil and Gas	Carstairs, Alberta	Expanding to 195	Early 1969		
	Caroline, Alberta	18	July 1968		
	Kaybob, Alberta	1170	Nov. 1968		
	Brazeau River, Alberta	35.6	Nov. 1968		
	Garrington, Alberta	—	Aug. 1968		
Imperial Oil	Sarnia, Ontario	60	Complete		500,000
Pan American Petroleum	East Crossfield, Alberta	1660	Under construction		
	Bigstone, Alberta	—	Under construction		
Shell Canada	Waterton, Alberta	Expanding to 1200	Early 1968		
	N. Burnaby, British Columbia	16	1968		600,000
	Jumping Pond, Alberta	—	Under construction		
LATIN AMERICA					
Petroleo Brasileiro	Rio de Janeiro, Brazil	33	1968	Petroleum refining	350,000
	Sao Mateus do Sul, Brazil	50		Petroleum refining	
Petroleos	Veracruz, Mex.	120	Mar. 1970	Petroleum refining	
	Madero, Mex.	55	Complete	Petroleum refining	
Shell Curacao	Curacao	50	Under construction	Petroleum refining	300,000

The smallest sulfur plant that is justified by the economics of sulfur recovery depends on a number of variables. Units have been built and operated economically with as small a capacity as 4 tons per day.[19] In areas where local air pollution regulations limit the amount of sulfurous gas emissions to the atmosphere, the least expensive air pollution control method may be a low-capacity sulfur plant. Fortunately, even the smallest modern refineries are capable of producing enough H_2S to support an economically operated sulfur plant.

Typical sulfur plant costs are shown in Table 5–8 for 20- and 40-ton plants. These estimates are not firm since costs vary with plant location and existing facilities.

Table 5–8. TYPICAL TWO-STAGE SULFUR PLANT COSTS

Plant size:		
Capacity, long tons/day	20	40
Production, long tons/yr.	6,570	13,140
Investment:		
Plant cost	$287,000	$330,000
Working capital, 15 percent	$ 43,000	$ 50,000
Total investments	$330,000	$380,000
Operating costs, $/long ton sulfur		
Depreciation, 10 per cent of cost	4.30	2.52
Taxes and insurance, 3.0 percent	1.29	0.75
Total fixed costs	5.59	3.27
Operating labor	4.68	3.08
Supervision and clerical	3.72	2.16
Maintenance	4.02	2.86
Supplies, estimated	0.54	0.54
Payroll, overhead	1.56	1.02
Water	0.42	0.42
Power and fuel	0.75	0.75
Total direct costs	15.69	10.83
Total cost at plant, $/long ton	21.28	14.00
Credit for steam, $/long ton	1.00	1.00
Net cost at plant, $/long ton of sulfur	20.28	13.00

The estimated costs of two-stage sulfur plants operated on an H_2S-rich stream are indicated on the curve in Figure 5–5.[26] A two-stage plant is ordinarily capable of operating with an H_2S-to-sulfur conversion efficiency of 90 percent.

5.3 SULFURIC ACID PLANTS

5.3.1 Introduction

Sulfuric acid production has grown rapidly in the past few years, as shown Table 5–9. The 1967 production of over 28 million tons of sulfuric acid (largest mineral acid industry in the United States) resulted in the atmospheric emission of approximately 600,000 tons of SO_2.

Table 5–9. SULFURIC ACID PRODUCTION (100 percent basis)
[10^6 tons]

	1963	1964	1965	1966	1967 (est.)
Contact process	19.4	21.4	23.5	27.5	27.3
Chamber process	1.5	1.5	1.3	1.2	0.9
Total	20.9	22.9	24.8	28.7	28.2

Tight sulfur supply may, however, limit the production of sulfuric acid in the future. The modern trend is toward construction of giant plants. A 2000-ton-per-day, single-train sulfuric acid plant has recently been built.[27] Several others, each of which will produce more than 1500 tons of acid per day, are under construction.

5.3.2 Sulfuric Acid Manufacturing

The principal raw materials used for the manufacture of sulfuric acid are elemental sulfur, sulfides (iron, copper, and zinc), H_2S from sour gases, and spent sulfuric acid from various chemical processes.[4] Elemental sulfur

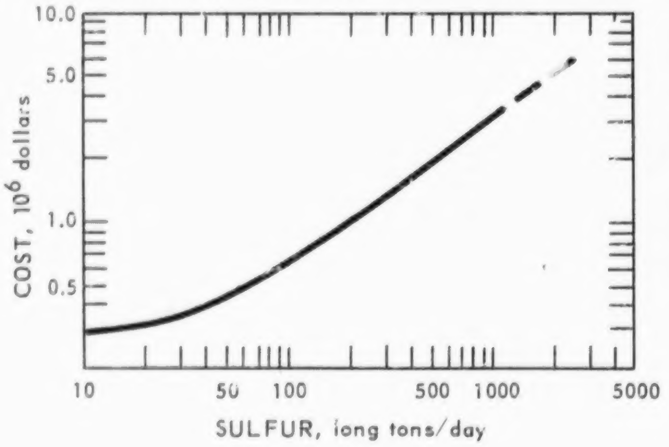

Figure 5-5. Estimate of investment cost for two-stage converter sulfur plant.

is the raw material from which about 70 percent of all sulfuric acid produced in the United States is derived.

Two processes are currently used to produce sulfuric acid, the contact process and the almost obsolete chamber process. Fundamentally, these processes are similar: both initially burn sulfur, with a controlled mount of excess air, producing SO_2 gas; both catalytically oxidize the SO_2 to SO_3; both must control the heat balance of the reaction to secure the desired equilibrium; and both use an absorber as the final step before the tail gases enter the atmosphere. The chamber process produces weaker acid (77.7 percent) and uses nitrogen oxide gas a catalyst; the contact process, which uses a vanadium pentoxide catalyst, produces 98 to 100 percent acid and various grades of oleum.

Since the chamber process is obsolete, no plants of this type have been built for many years. A flow chart of a typical sulfur-burning contact plant is shown in Figure 5–6.[18] Dry air is used to burn sulfur to SO_2 with a controlled amount of excess air. The SO_2, at a concentration of 7 to 10 percent, passes through a waste-heat boiler and gas filter before entering a four-stage converter. Each stage of the converter consists of a fixed bed of pelletized vanadium pentoxide catalyst. When the gas passes through this catalyst, SO_2 reacts exothermically with excess air to form SO_3. Heat exchangers are used to lower the temperature of the gas to its optimum conversion temperature before the gas enters the outer catalyst stages. Rarely are more than four stages used. Sulfur trioxide gas mixture leaving the fourth stage of the converter is cooled to approximately 475°F and enters the absorber, where the SO_3 is almost all absorbed by counter-current contact with 98 to 99 percent sulfuric acid. Sulfur dioxide is not absorbed in this solution. The tail gas from the absorber with unconverted SO_2, unabsorbed SO_3, and acid mist is normally discharged directly into the atmosphere.

When oleum is produced, the converter gases containing 7½ to 10½ percent SO_3 are absorbed in 98 percent sulfuric acid circulated through an oleum tower until the desired acid strength is obtained. Because of free SO_3 content of oleum, there is an increase in SO_3 emissions to the atmosphere when oleum is produced.

5.3.3 Emissions

The extent of SO_2 emissions in large measure depends upon efficient operation and a plant design that ensures a high rate of conversion of SO_2 to SO_3 and subsequent absorption. The heart of the contact plant is the converter, where a number of factors determine the quantity and concentration of SO_2 emissions. Some of these factors are: (1) concentration of the entering SO_2, (2) ratio of oxygen to SO_2, (3) number of catalyst converter stages, (4) arrangement and volume of catalyst, (5) catalyst

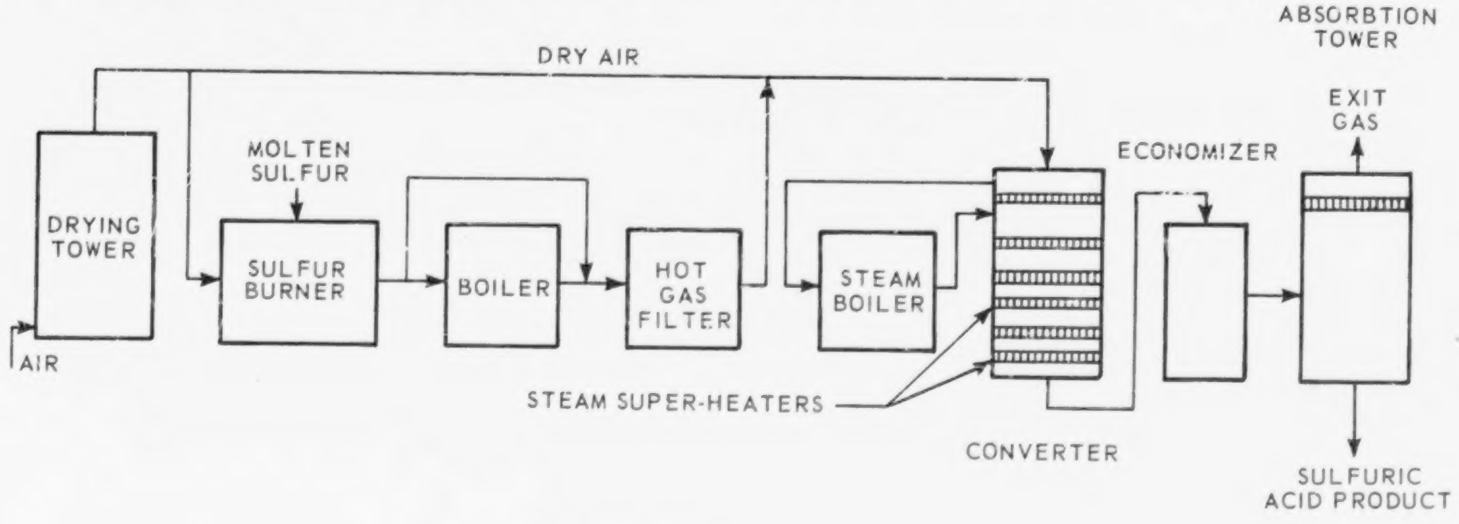

Figure 5-6. Flow chart of a typical sulfur-burning contact sulfuric acid plant.

efficiency, (6) gas uniformity, (7) impurities in the entering gas, and (8) temperature control.[1] Normal operation will obtain an SO_2 conversion efficiency of 96 to 98 percent in a well designed, modern, contact plant, and will result in emissions of from 25 to 40 pounds of SO_2 per ton of acid produced, as shown in Figure 5-7. Exit gas concentrations of SO_2 in well operated plants vary from about 2000 to 3500 parts per million, as shown in Figure 5-8.[4] Under certain operating conditions, e.g., during startups, when the catalyst has not been sufficiently preheated, or under high-capacity operations or plants upsets, these concentrations could exceed 5000 parts per million as shown in Figure 5-8. Emissions from chamber plants vary from 25 to 30 pounds of SO_2 per ton of acid produced. Concentrations of sulfuric acid mist in the exit gas range from 3 to 15 milligrams per standard cubic foot for a contact plant, and 5 to 30 milligrams per standard cubic foot for a chamber plant. The concentration of unabsorbed SO_3 in the exit gas from a contact plant varies substantially, but is usually about 0.5 milligram per standard cubic foot. Sulfur trioxide mist, upon contact with atmospheric moisture, is hydrated and forms a visible, white, acid-mist plume.

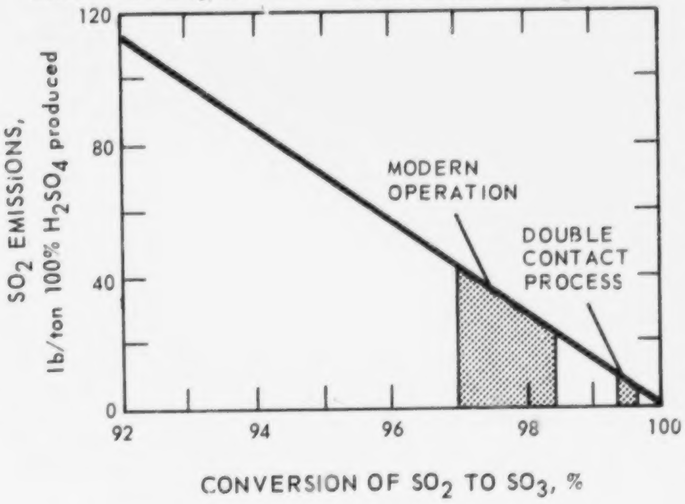

Figure 5-7. Sulfur dioxide emissions from contact plants at various conversion efficiencies (per ton of equivalent 100% H_2SO_4 produced).

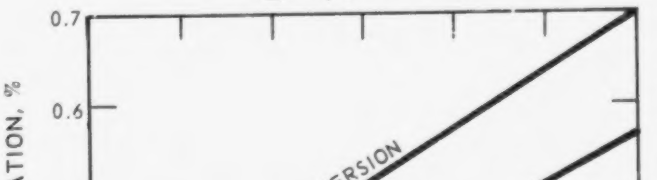

Figure 5-8. Concentration of SO_2 in exit gas at various conversion efficiencies.

5.3.4 Control Methods for Sulfur Oxides

Any factor that increases the conversion of SO_2 to SO_3 will naturally reduce SO_2 emissions. Conversion efficiencies greater than 99.7 percent have been claimed for the Bayer double-contact process.[28] This process is based on the principle that the conversion of SO_2 to SO_3 is improved if the equilibrium is shifted by absorbing the SO_3 formed in the early conversion stages and subjecting the remaining SO_2-bearing gas to a final conversion. In this process, the typical conversion system is modified by adding an intermediate absorbing tower just ahead of the fourth catalyst conversion stage. An additional heat exchanger also is required to cool the gases before they enter the intermediate absorber. The overall degree of conversion is improved because the remaining SO_2, freed from most of the SO_3, encounters a very high degree of conversion when once more reacted in the final fourth stage.

Figure 5-9 is a flow chart of the double-contact process.[28] Several double-contact plants have been in operation in Europe since the first one was installed in 1964. The double-contact system could be adapted to an existing contact plant; however, installation would be very expensive and has not yet been done in this country.

A similar scheme, called the Burkhardt S.A. process, also employs intermediate absorption. Burkhardt S.A. claims efficiencies of 99.0 to 99.6 percent in plants using brimstone sulfur as raw material.[29] This efficiency range will result in exit SO_2 concentrations of 500 to 1000 parts per million. No known installations of this process are presently in operation.

The advantage of the double contact and Burkhardt S.A. processes, beyond the reduction of SO_2 emissions, is that a greater conversion capacity can be obtained. This is accomplished not only by the higher conversion efficiency but also by allowing a higher concentration of SO_2 to enter tne converter. The double-contact plants used in Europe, instead of operating with 6.5 to 7 percent SO_2 from pyrites, now operate with up to 10 percent SO_2 inlet concentrations.[28]

Cost data show that the additional equipment investment is compensated by smaller equipment and higher sulfuric acid yields.[28] Additional capital expenditure of 10 to 15 percent is required to increase conversion efficiency from 98 percent in a typical new contact plant to 99.5 percent in the double-contact plant.[30] In evaluating the economics of a double-contact plant versus a typical contact plant, it is generally estimated that the additional revenue obtained from increased production achieved through higher yields will provide a payout period of about 5 years for the additional capital expenditure required for a duoble-contact plant. The payout period would be further decreased if a higher initial SO_2 concentration were used. For instance, a 140,000-ton-per-year sulfuric acid plant operating at a conversion rate of 98 percent would emit about 1750 tons of SO_2 per year; with double-contact conversion of 99.5 percent the plant would emit about 420 tons of SO_2 per year and produce more than 2000 additional tons of sulfuric acid.

A number of gas scrubbing systems are also available for removing SO_2. The ammonium sulfite-bisulfite scrubbing system pioneered years ago at Trail, British Columbia, has reduced SO_2 in the tail gas from as high as 0.9 percent to 0.03 percent. Recently, Dutch State Mines has spent $420,000 on a similar plant for the purification of tail gases resulting from the production of sulfuric acid and oleum. The DSM control system consists of passing the tail gases through an ammonia solution that retains 95 percent of the SO_2. The resulting ammonium bisulfite solution is used for the preparation of caprolactam.[31] Scrubbing systems reduce plume bouyancy and may cause a visible plume due to water vapor.

Sulfur trioxide, sulfuric acid mist, and spray in the exit gas can be controlled by a

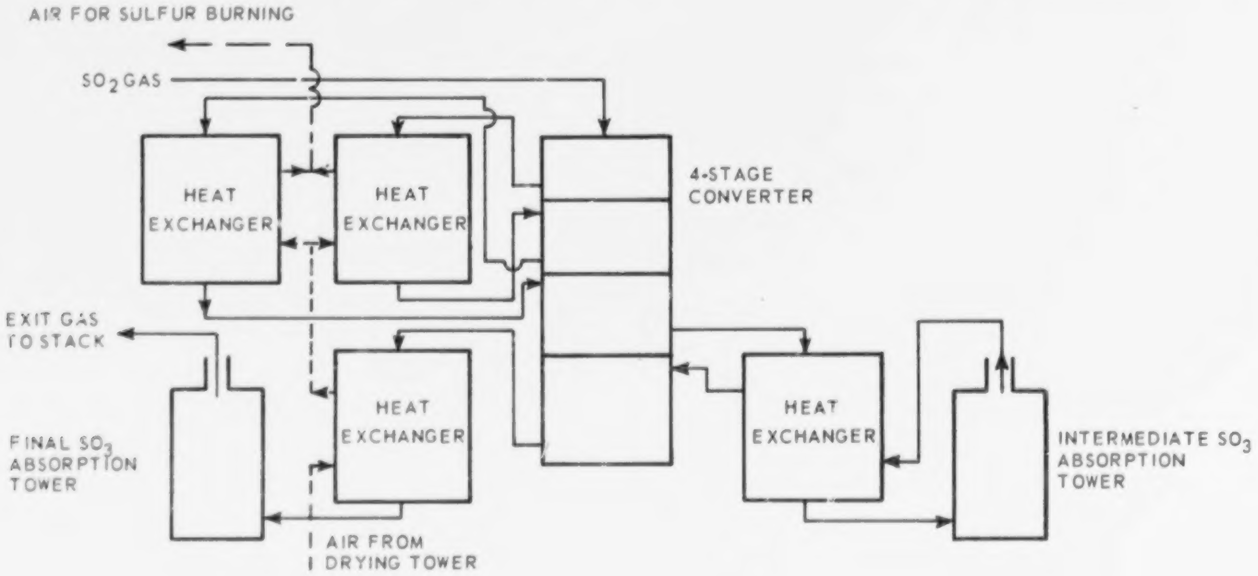

Figure 5-9. Flow chart for sulfur-burning double-contact plant with intermediate SO_3 absorption.

number of devices of varying costs and efficiencies. Some of these are wire-mesh mist eliminators, fiber mist eliminators, electrostatic precipitators, and packed bed separators. For a description of mist eliminators, refer to *Control Techniques for Particulate Air Pollutants.*

5.4 STEEL MANUFACTURING

5.4.1 Introduction

An integrated steel plant has coke manufacturing, blast furnace, and steel furnace facilities. Iron ore, which is received in the form of impure iron oxide, is reduced in the blast furnace to form metallic iron. Combustion of coke provides the reducing atmosphere in the furnace. The metallic iron (pig iron) is further refined to steel by reducing the impurities and adjusting the alloy content to specified levels. Pig iron is usually refined to steel in open-hearth furnaces (oxygen lanced and non-oxygen lanced), basic oxygen furnaces, and electric arc furnaces. In both blast furnaces and steel making furnaces, a slag is formed which floats on the molten metal and removes the impurities.

Sulfur dioxide emissions from steel plants are produced primarily from sintering, coke manufacture, and combustion operations.

5.4.2 Sintering

Agglomerating processes are used on blast-furnace feed for beneficiating ore and salvaging recovered dust. The primary purpose of agglomeration is to improve the permeability of the blast-furnace burden, hence improving the gas-solid contact and rate of reaction, and reducing the coke consumption. A secondary purpose is to improve the movement of the burden in the blast furnace as melting progresses and, thus, reduce the quantity of dust emitted from the furnace. Sintering and pelletizing are the primary types of agglomerating processes used on iron ore. Sintered materials include iron oxide fines from cyclones and electrostatic precipitators, mill scale from metal working operations, metal turnings, and light scrap. Fluxes are sometimes added for better control of the properties of the sinter.[32] Adding limestone flux to the sinter increases hot metal production and decreases coke consumption; raw limestone fed to the blast furnace is, of course, correspondingly decreased.[33]

Sintering is done on a belt of perforated pallets moved by sprockets about 100 feet apart.[34] Iron ore fines and coke breeze, or coal, are placed on the pallets, and the charge is ignited as it passes through a short ignition section of the furnace. Combustion air is pulled downward by a fan, through the burning charge, through the perforations in the steel pallets, into the windbox, and in most cases out the stack. The coke burns out of the charge, and the hot clinker is removed from the belt and used for blast-furnace feed.

Sulfur emissions from sintering come from the iron ore and the coke. Iron ores used in the United States are quite low in sulfur, usually under 0.03 percent. Coking coals usually contain less than 1 percent sulfur, about 30 percent of which is liberated by by coking. The sintering operations may remove as much as 70 percent of the sulfur in the total charge.[35] Within limits sintering is a good blast-furnace feed-desulfurizing procedure, especially for high-sulfur charges. Most of the sulfur entering the blast furnace is reduced to sulfide and combines with the slag. The blast furnace is operated to minimize the sulfur content of pig iron. Hydrogen sulfide is liberated from the slag, and some of the slag sulfide content is gradually oxidized to SO_2 by ambient oxygen.

5.4.3 Coke Ovens

Iron and several other important metals are recovered from their ores by high-temperature reduction. Wood charcoal was once used as the reducing agent, but it has long since been replaced by coke, which is now the main metallurgical reducing agent. Production of a ton of pig iron from a blast furnace requires about 0.7 ton of coke.[36] About 90 percent of the United States coke output is used in metallurgical operations.[37]

Coke is the solid material remaining after distillation of certain bituminous coals in the absence of air. Because sulfur is very deleterious to the quality of steel and is difficult to remove in blast furnace or refining operations, low-sulfur coals are used whenever available and, indeed, command a premium price for metallurgical purposes.

Conventional coking is done in long rows of slot-type coke ovens into which coal is charged through holes in the top of the ovens.[36] Coke oven gas or other suitable fuel is burned in the flues surrounding the ovens, to furnish heat for coking. Flue temperature is about 2600°F and the coking period averages 17 to 18 hours.[37] At the end of the coking period, incandescent coke is pushed out of the furnace into quenching cars and carried to a quenching station, where it is cooled with water sprays.

Volatile matter from the distillation contains materials ranging from hydrogen and methane to high-molecular-weight materials such as tars. In addition to hydrocarbons, organic compounds of sulfur and nitrogen are present. Because the coke oven environment contains strong reducing agents, sulfur is present as H_2S and in other reduced forms, as carbon disulfide. Tars are separated from the hot coke-oven-gas stream by condensation. Ammonia and organic gases are removed by water sprays and by absorption in sulfuric acid. Benzene homologues are removed by absorption in straw oil. After removal of by-products, the resulting coke-oven flue gas consists mainly of hydrogen, methane, and carbon monoxide. Up to 50 percent of the sulfur in the original coal is volatilized, and much of it remains in the coke-oven-flue gas unless removed by special treatment.

The usual distribution of the sulfur from the original coal to coke oven products is shown in Table 5-10.[39] The debenzolized coke-gas may contain as much as 0.7 percent H_2S by volume, and this gas will generate SO_2 when used as fuel.

Table 5–10. DISTRIBUTION OF SULFUR IN COKE OVEN PRODUCTS[39]

Coke oven products	Percent of original sulfur in coal
Coke	50–65
Gas (as H_2S)	25–30
CS_2, thiophene, and other organic compounds	1–1.5
Tar and ammonia liquor	2.4–3.5

Pyritic sulfur in coal is reduced in the coke oven to form H_2S:

$$FeS_2 + \text{organic heat} \longrightarrow FeS + H_2S$$

Therefore, pyrite removal from coal is an aid to reduction in emissions of sulfur oxides from subsequent combustion of coke-oven gas.

In a coke plant, SO_2 emissions originate from the fuels burned to heat coke ovens (including coke-oven gas) and from leaks around the ovens. Oven leaks release gases containing sulfur compounds. The leaking gases are at high temperatures so that when they issue into the air, they burn immediately to form SO_2 from any sulfur compounds present. SO_2 is also emitted when the incandescent coke is pushed from the oven and is transported to the quenching tower. Most of the sulfur in the coke is released into the slag when the coke is subsequently used in the blast furnace.

Escape of gas from coke ovens is caused by charging coal, removing coke ("pushing"), and by leaks at many points around the ovens. Control of gaseous emissions, therefore depends upon speed, organization, and maintenance relative to oven operations, and coke-oven-gas treatment to remove sulfur compounds before using the gas as fuel.

Coke oven gas contains 300 to 500 grains of sulfur per 100 cubic feet of gas, or 0.5 to 0.8 percent sulfur by volume, mainly as H_2S. Combustion of this gas results in SO_2 emissions. Various methods have been used to remove H_2S from coke-oven gas. One method involves passing the coke-oven gas through a sodium carbonate absorber.[40] The resulting solution is regenerated by passing through a heated vacuum tower. The sulfur content of the gas can be reduced to about 50 grains per 100 standard cubic feet by this method if the CO_2 content for the coke-oven gas is relatively low. In the past, stripped H_2S was often vented, or burned to SO_2. Another method for disposing of the stripped H_2S is to utilize the burned gas for feed to a sulfuric acid plant, or to add it to the main gas feed of a sulfuric acid plant.[41] Preliminary treatment is generally necessary to remove impurities such as hydrogen cyanide.

A second coke-oven-gas treating process removes H_2S by absorption in sodium thioarsenate.[11] The rich thioarsenate solution is then heated and sent to a second tower, where the solution is regenerated with air and elemental sulfur is eliminated. Another process for H_2S removal involves scrubbing the gas with an alkaline solution of anthraquinone and sodium vanadate.[12] The H_2S is oxidized to elemental sulfur, and the solution is regenerated by oxidation with air. No cost data were found pertaining to coke-oven operation or gas cleaning.

Slot-type coke ovens currently being designed include the following features designed to speed operations and minimize leaks:

1. Better designed and thinner-walled heating flues to improve heat transfer and minimize cool spots and undercoking. This results in a cleaner pushing operation.
2. Improved refractories with less spalling and cracking. These refractory defects cause warping of metal furnace parts, gas leaks into flue systems and chimneys, and voids, which fill with undercoked coal and cause smoke during pushing.
3. Gas-tight, self-sealing oven doors, which no longer require manual sealing with clay.
4. Mechanical cleaners or self-sealers for doors and for top-charging hole covers. A few grains of sand on a metal seat can cause appreciable leakage of hot gases.
5. Sealing sleeves for levelling bars. Levelling bars are used to even out the oven charge to allow free passage of gas over the charge into the gas collector main.
6. Mechanical removal of top coal-charging lids and means to charge all three holes of an individual oven rapidly and simultaneously, with gas recovery mains in operation.

A method for enclosed pipeline charging of preheated coal is also being deveolped. An enclosed system eliminates the possibility of emission during charging.

It is evident that emissions from coke ovens can actually be reduced by good organization and planning of operations, proper scheduling, careful training of operators in battery cleanliness and attention to detail, and incentives for smokeless operation.

Efforts have been made to develop a satifactory continuous coking operation because continuous operations are inherently tighter and more easily controlled. One process investigated is fluid-bed pyrolysis designed to upgrade sub-bituminuous coals.[13] The char produced might be briquetted for blast furnace feed. Continuous coking has been carried out to a limited extent in a manner similar to belt sintering, in which the amount of air passed through the coal is sufficient to cause combustion of the volatile matter without undue combustion losses of coke. Currently, however, no practical substitute for the slot coke oven exists.

Coke is still produced in beehive-type ovens in the United States on a very limited scale. Because this obsolete process does not recover any of the volatile gases generated in the coking process, it causes considerable air pollution. The only practial control method is to replace the ovens with well-designed slot-type ovens with by-product gas recovery systems.

5.5 PULP AND PAPER MILLS

5.5.1 Introduction

Pulp and paper production is one of the ten largest industries in our country.[14] Per capita demand for paper products is nearly 530 pounds per year.[15] The manufacture of paper and related products can be divided into two phases, pulping of wood and production of paper from pulp.

The manufacture of paper from pulp ordinarily results in only small quantities of atmospheric pollutants.

In the pulping process, wood of various types is reduced to fiber, sometimes bleached, and then dried in preparation for making the final product at the paper mill. Most pulp mill processes use some type of cooking liquor to dissolve lignins in the wood and free the wood fibers. In many cases, to make this process economical, spent cooking liquor is recovered, usually by some process involving combustion. It is mainly in recovery processes that potential air pollutants are generated. The major pollutants from pulp mills are particulates, odorous sulfur compounds (H_2S, methyl mercaptan, dimethyl sulfide, dimethyl disulfide, and other organic-sulfur compounds), and SO_2. Which pollutants are emitted in significant amounts depends on the type of recovery process employed and the degree to which control equipment is used.

There are three major pulping and recovery processes used in the United States (sulfate, sulfite, and semichemical), and they account for nearly 80 percent of the pulp produced in this country. The remaining 20 percent of the pulp is produced by a number of small mills using various specialized processes. Table 5-11 lists these processes, the quantity of pulp produced by each, and their potential atmospheric emissions.

The sulfate or kraft process has created the greatest pulp manufacturing air pollution problem, mainly because of the large quantity of visible particulate and the highly odorous nature of the sulfur compounds emitted. Sulfur dioxide emissions from the sulfate process are minor, but those from the sulfite and semichemical processes are potentially major. Sulfur dioxide emissions can be controlled and, in the case of the sulfite and semichemical processes, provide an economic benefit from sulfur recovery.

5.5.2 Sulfate (Kraft) Process SO_2 Emissions and Control

Sulfate pulping involves cooking wood chips in a caustic soda and sodium sulfide solution. The process name comes from the fact that sodium sulfate is used as the makeup chemical. A flow chart for a typical digestion and chemical recovery process is shown in Figure 5–10.[46]

Sulfur dioxide emissions from the sulfate recovery process are not great. The significant sources of SO_2 are the recovery furnace, lime kiln, and smelt dissolving tank. Table 5–12 shows the range of SO_2 emissions encountered in various sulfate mills.

Table 5–12. RANGES OF SO_2 CONCENTRATIONS IN STACK GAS FROM TWO KRAFT MILLS[46]

Source	SO_2, ppm	SO_2 per ton of air dried pulp, lb
Recovery furnace	4–798	2.4–13.4
Lime kiln	0–169	0.1– 0.3
Dissolving tank	0.5–70	0.0–0.14

Control devices specifically for SO_2 are not used at sulfate mills because of the relatively small SO_2 concentrations and the greater need to control other pollutants.

Sulfur dioxide emissions are, however, controlled as a secondary effect of controlling odorous and particulate emissions. One recent study of recovery furnace operation has shown that sufficient secondary air, turbulence in the secondary zone, and liquor spray-pattern can substantially reduce emissions of odorous sulfur compounds and SO_2.[47] Tables 5–13 through 5–15 show the effects of operating variables on SO_2 emissions. Most recovery

Table 5-11. PULP MILL PROCESSES AND POTENTIAL ATMOSPHERIC EMISSIONS IN 1966

Type of pulp mill	Number of mills in U.S.	Total annual pulp production, 10^6, tons	Air pollutant emissions	
			Major	Minor
Sulfate (kraft)	111	23.6	Particulate, odorous sulfur compounds (sulfides and mercaptans)	Sulfur dioxide
Sulfite	50	2.7	Sulfur dioxide	Particulates [a]
Semichemical	42	3.1	Hydrogen sulfide	Particulates [a]
Other [b]	173	6.2	No significant emissions	No significant emissions

[a] May be major source once other pollutants are controlled.

[b] Includes ground wood, soda pulp, and roofing pulp mills.

Table 5–13. EFFECTS OF FURNACE SECONDARY AIR ON SO_2 AND OTHER SULFUR COMPOUND EMISSIONS[47]

Secondary air, percent	Excess O_2, percent	SO_2, ppm	H_2S, ppm
28.5	1.4	96.7	24.6
30.0	1.2	53.0	12.6
36.5	2.6	0.1	0.007
41.0	3.4	0.2	0.012

Table 5–14. EFFECTS OF TURBULENCE ON FURNACE GASEOUS EMISSIONS[47]

Velocity at secondary airport outlet, ft/sec	SO_2, ppm	H_2S, ppm
180	0.2	0.012
65	47.1	84.5

furnaces do not, however, operate at optimum conditions from an air pollution standpoint, and odorous emissions continue to be a problem at many mills.

Table 5–15. EFFECTS OF LIQUOR SPRAY PATTERN ON FURNACE GASEOUS EMISSIONS[47]

Type spray	SO_2, ppm	H_2S, ppm
Coarse	0.08	0.0
Fine	9.8	0.37

Scrubbers are normally used on lime kilns and dissolving tanks to control particulate matter and some odorous emissions. These control devices also reduce SO_2 emissions.

5.5.3 Sulfite Process SO_2 Emissions and Control

Sulfite pulping is an acid-base process for dissolving the lignin bonding material from wood chips. The cooking liquor is produced by reacting SO_2 with one of four bases (ammonium, calcium, magnesium, or sodium) in an absorption device. The bisulfite solution that forms is used as cooking liquor for wood chips in a digester.

A sulfur burner is the usual source of SO_2

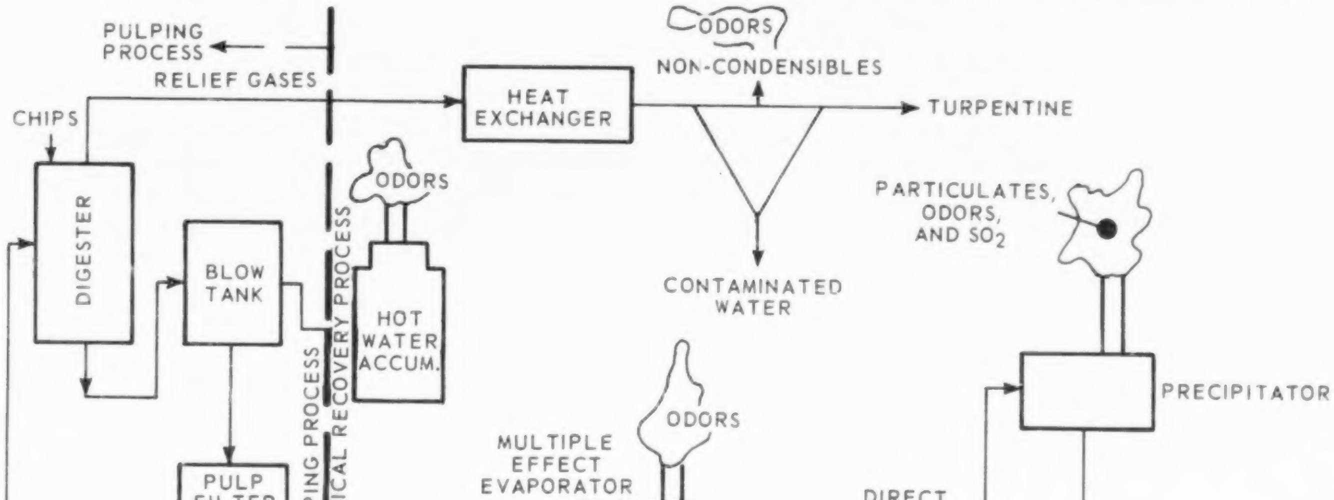
PULPING PROCESS
RELIEF GASES
CHIPS
DIGESTER
BLOW TANK
PULP FILTER
PULP
ODORS
HOT WATER ACCUM.
PULPING PROCESS
CHEMICAL RECOVERY PROCESS
HEAT EXCHANGER
ODORS
NON-CONDENSIBLES
TURPENTINE
CONTAMINATED WATER
PARTICULATES, ODORS, AND SO_2
PRECIPITATOR
MULTIPLE EFFECT EVAPORATOR
ODORS
DIRECT CONTACT EVAPORATOR
RECOVERY FURNACE
SULFUR AND Na_2SO_4
WHITE LIQUOR
$CaCO_3$
PARTICULATE SO_2
LIME KILN
FILTER
CaO
CAUSTICIZER
GREEN LIQUOR
SMELT ($Na_2S + Na_2CO_3$)
PARTICULATE ODORS SO_2
WATER
CHEMICAL RECOVERY PROCESS

Figure 5-10. Typical sulfate pulping and recovery process.

for the calcium-, sodium-, and ammonia-base sulfite processes. Methods for absorption of relatively strong SO_2 gas in the appropriate base are fairly well established. Sulfur dioxide emissions from absorption systems can, however, be significant unless proper process control and maintenance are practiced. It is imperative that proper flow-rates, temperatures, and concentrations of the SO_2 gas and absorption solution be maintained to minimize atmospheric emissions. Keeping the absorption system operating at optimum conditions may require some added expenditure in the form of extra operating and maintenance personnel.

Gases from the digester and blow tank are another source of SO_2. The sulfur content of these gases can be controlled by passing them through condensers and absorption towers or caustic scrubbers. One mill has reported a net saving of over $250,000 per year from recovery of sulfur by installation of a condenser and absorber to control SO_2 emissions from blow tanks.[48]

Much of the spent sulfite cooking liquor has been sewered in the past, but greater emphasis is being placed on burning the liquor to reduce stream pollution, recover chemicals, and generate steam. The spent sulfite cooking liquor, being relatively high in organic sulfur compound, is potentially a large combustion source of SO_2. Control of such emissions is possible and practical since recovered SO_2 in the form of H_2SO_4 can be used as make-up chemical in the process. The magnesium-base sulfite liquor is most suitable for burning since the magnesium and SO_2 can be efficiently recovered. Most new sulfite mills in this country are of the magnesium-base type for this reason. Spent ammonium-, calcium-, and sodium-base liquors can be burned, but only SO_2 can be efficiently recovered, since the spent liquor is either destroyed or changed in the combustion process.

Economical operation of the sulfite process requires efficient recovery of SO_2 from the combustion gases, since concentrations of over 1 percent SO_2 (10,000 parts per million) result from liquor combustion. With relatively poor recovery (less than 90 percent), SO_2 emissions can be as high as 60 pounds per ton of pulp. With 90 percent recovery, SO_2 emissions can be reduced to approximately 1000 parts per million, or 20 pounds per ton of pulp.[49] Another study states that over 98 percent recovery is possible with three-stage venturi absorption, resulting in stack emissions of about 300 parts per million SO_2, or 3 pounds per ton of pulp.[50]

Figure 5–11 shows a typical magnesium-base, chemical-digestion-and-recovery system with air pollution control devices installed to control SO_2 and odorous sulfur compound emissions from the blow tank, multiple-effect evaporators, and recovery furnace. Sulfur dioxide emissions from the combustion process are recovered by efficient absorption in the scrubber and the three absoprtion towers.

5.5.4 Neutral Sulfite Semichemical SO_2 Emissions and Control

The neutral sulfite semichemical pulp process, the most widely used semichemical process, normally uses sodium sulfite and sodium bicarbonate as a cooking liquor. The spent cooking liquor can be burned with chemical recovery.

Large quantities of SO_2 are generated in the combustion of the spent liquor. Figure 5–12 shows how SO_2 can be used to convert the smelt from the combustion process to fresh cooking liquor. With the proper operation of this system, little SO_2 or H_2S will be emitted to the atmosphere.

Small amounts of SO_2 and odorous sulfur compounds are released from the digester blow gases and multiple-effect evaporators used to concentrate spent liquor prior to burning. These emissions can be effectively controlled by scrubbing.

5.5.5 Steam and Power Boiler Atmospheric Emissions

Many pulp and paper mills have auxiliary power boilers to produce process steam. When these units are fired by coal or residual oil, SO_2 emissions can be quite large, larger in fact than any SO_2 emissions from chemical recovery processes.

One unique control method for SO_2 emissions from boilers at a kraft mill has been proposed.[51] The method involves scrubbing power-boiler flue gases with black liquor from the kraft process. The SO_2 absorbed in the liquor adds sulfur to the cooking liquor. Process makeup sulfur is reduced and SO_2 is removed from stack gases by a process that could provide an economic return. A sodium carbonate scrubbing system has also been proposed.[52]

5.6 WASTE DISPOSAL

5.6.1 Coal Refuse

5.6.1.1 Introduction—Coal refuse is waste coal, rock, shale, culm, boney, slate, clay, and related materials associated with a coal seam, which are removed from the mine in the process of mining coal or which are separated from coal during cleaning and preparation. Coal refuse is often deposited in large piles near mines and coal cleaning plants. These materials usually contain large quantities of sulfur, in the form of "pyrites."[53,54]

Coal refuse may be fired intentionally, accidentally, or by spontaneous ignition. Ignition is more likely to occur if the waste pile contains extraneous organic material like wood or garbage. Camp fires or brush fires often furnish the ignition. Spontaneous firing occurs by slow oxidation of the coal. Water may contribute to ignition by the heat of wetting, depending on the physical nature of the coal and on humidity.[55]

Sulfur dioxide is produced from the oxidation pyrites in the coal:

$$FeS_2 + 3O_2 \longrightarrow FeSO_4 + SO_2.$$

The actual reactions going on in the pile are quite complex. Another reaction is:

$$2FeS_2 + 2H_2O + 7O_2 \longrightarrow 2FeSO_4 + 2H_2SO_4.$$

The sulfuric acid produced may liberate H_2S from the pyrites. This H_2S may further react:

$$2H_2S + SO_2 \longrightarrow 3S + 2H_2O.$$

Sulfur is often observed on burning waste piles, and the odor of H_2S is often noticeable.

Air samples taken in a community adjacent to a burning coal waste pile showed average hourly SO_2 levels ranging from 0.4 to 3.0 parts per million with peak levels from 0.6 to over 4.5 parts per million, depending

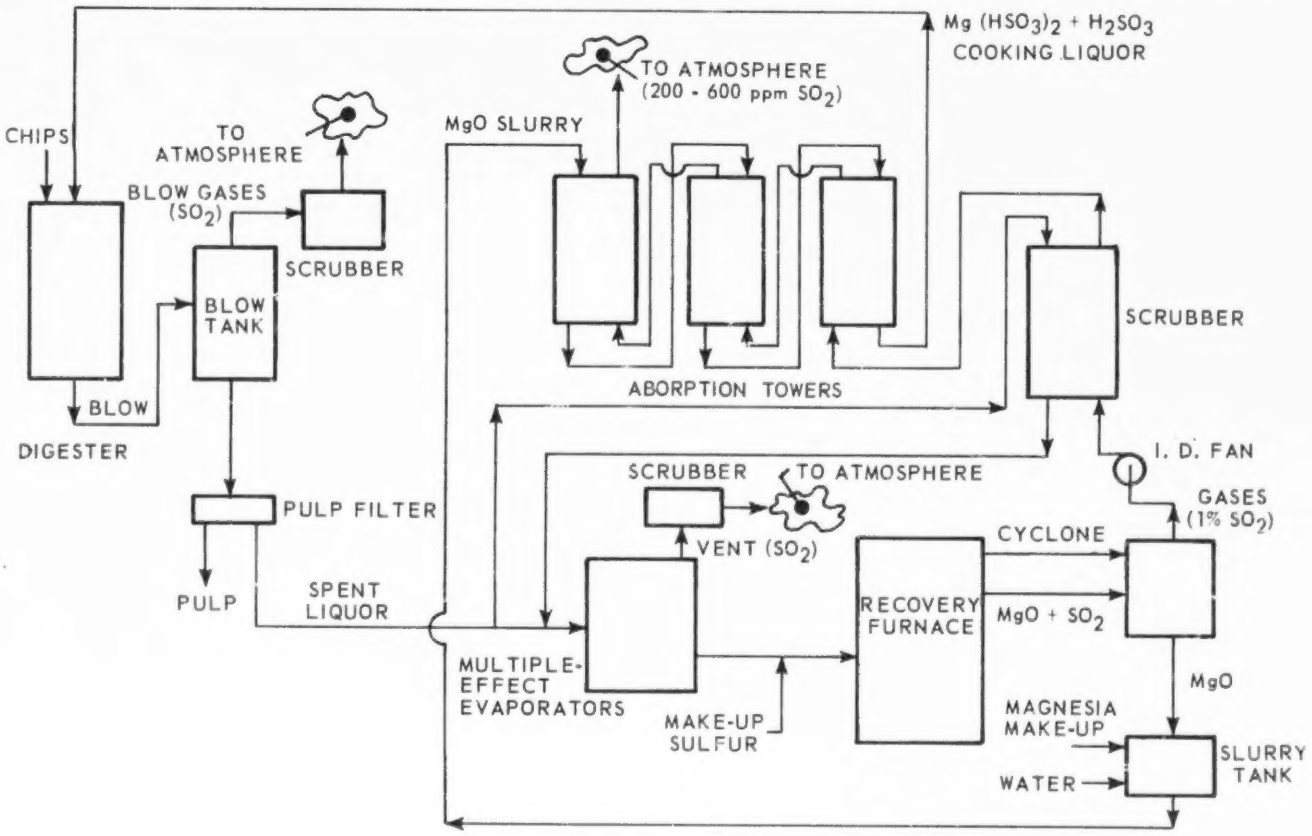
Mg (HSO3)2 + H2SO3
COOKING LIQUOR
TO ATMOSPHERE
(200 - 600 ppm SO2)
CHIPS
TO
ATMOSPHERE
MgO SLURRY
BLOW GASES
(SO2)
SCRUBBER
BLOW
TANK
SCRUBBER
BLOW
DIGESTER
ABORPTION TOWERS
I. D. FAN
SCRUBBER
TO ATMOSPHERE
GASES
(1% SO2)
PULP FILTER
VENT (SO2)
CYCLONE
PULP
SPENT
LIQUOR
RECOVERY
FURNACE
MgO + SO2
MULTIPLE-
EFFECT
EVAPORATORS
MgO
MAKE-UP
SULFUR
MAGNESIA
MAKE-UP
WATER
SLURRY
TANK

Figure 5-11. Typical mangesium-base chemical pulping recovery process.

on meteorological conditions.[53] Levels of H_2S, measured at another time, varied from 0.1 to 0.4 part per million.

5.6.1.2 Control Methods and Costs—Methods of air pollution control for coal waste piles consist of preventing or extinguishing fires. The method used should be designed for the particular problem at hand and will vary from one situation to another.

Among many methods investigated for extinguishing coal refuse fires are: cooling and repiling the refuse; sealing with impervious material (such as a blanket of well-compacted waste and a layer of clay); injecting a slurry of limestone or other noncombustible; and sealing top and sides with coal cleaning plant sludge. If the voids within the pile can be filled with inert materials, combustion will cease.

Prevention of coal waste pile fires is fostered by proper site selection and piling, and by ensuring the absence of wood, underbrush, paper, and other such combustibles. Trespassers should be kept away from the piles.

Among methods for handling new waste and non-burning waste piles are: coal recovery (reducing the amount of combustibles)[56]; weathering for initial oxidation followed by layering and compaction; and design of the waste piling to fit topography and the material so that future ignition is minimized. The following processes are examples of this last method:

1. Contouring the disposal valley and using earth to seal the down-valley face of the deposited waste.[54]
2. Crushing large rocks, so that there will be the proper distribution of intermediate- and small-sized particles for compaction into an impervious pile.

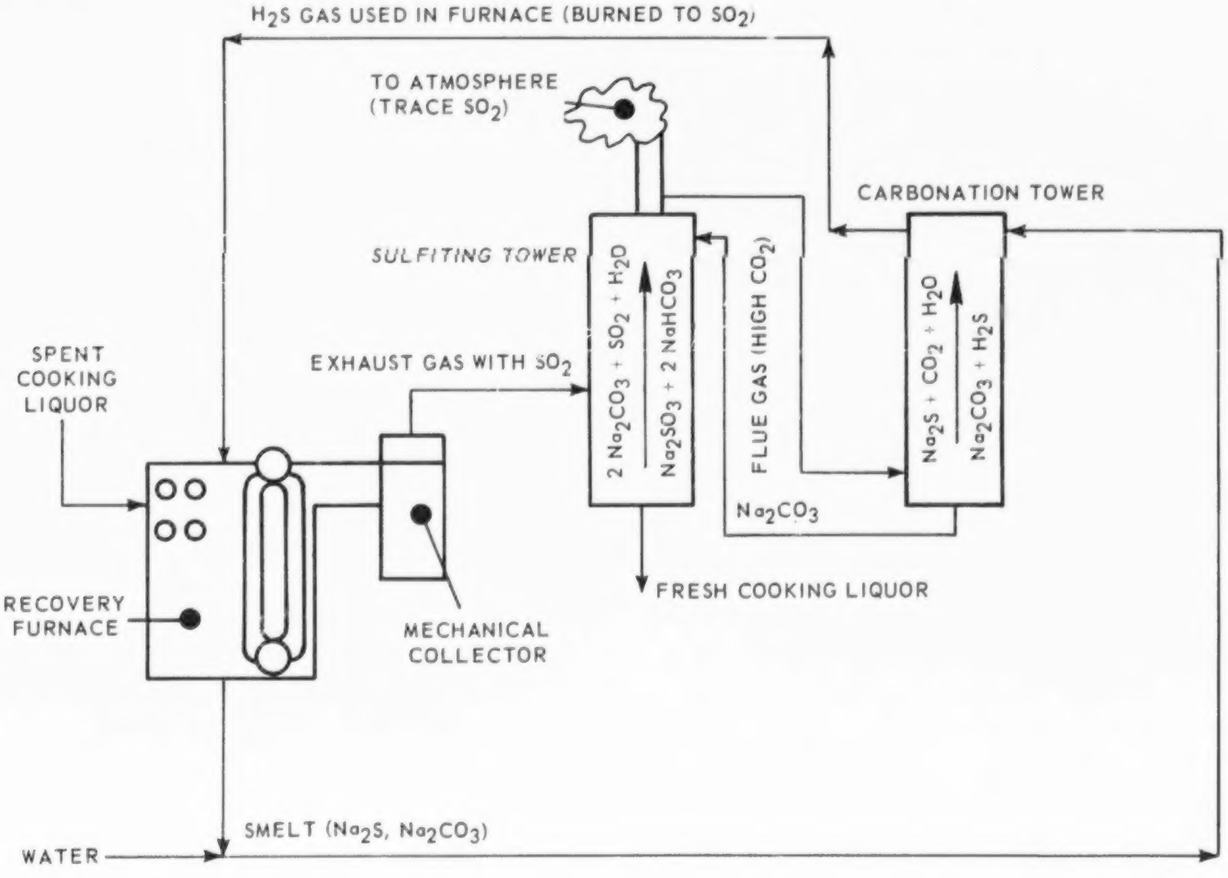
H_2S GAS USED IN FURNACE (BURNED TO SO_2)
TO ATMOSPHERE (TRACE SO_2)
CARBONATION TOWER
SULFITING TOWER
SPENT COOKING LIQUOR
EXHAUST GAS WITH SO_2
$2 Na_2CO_3 + SO_2 + H_2O$
$Na_2SO_3 + 2 NaHCO_3$
FLUE GAS (HIGH CO_2)
$Na_2S + CO_2 + H_2O$
$Na_2CO_3 + H_2S$
Na_2CO_3
RECOVERY FURNACE
MECHANICAL COLLECTOR
FRESH COOKING LIQUOR
SMELT (Na_2S, Na_2CO_3)
WATER

Figure 5-12. Typical recovery system for neutral sulfite - semi-chemical liquor.

3. Terracing of waste piles and filling in the terraces with sealing material such as clay to form a thick seal all around the pile.[57]
4. Contouring deep trenches around disposal hills in hilly terrain. Waste is dumped and compacted by trucks operating on it. When the first trench is filled, a second is superimposed by hill-side excavation on a contour just above it, and so on. One variant of this procedure uses excavated soil to cover the outside face of the pile as the work progresses uphill.

Demonstration projects cosponsored by the National Air Pollution Control Administration have indicated that costs of extinguishing coal waste pile fires can be expected to range between $0.25 and $1.25 per cubic yard.[53,58] Cost of preventing these fires by compacting, layering, and contouring would be about $1.00 per ton of refuse, based on the cost of sanitary landfills. A rough estimate, based on the dimensions of burning coal-mine refuse banks, indicates a total of over 1 billion cubic yards of such burning banks in the United States.[59]

5.6.1.3 Future Plans and Research—The National Air Pollution Control Administration has recently cosponsored 15 demonstration projects on extinguishing culm-pile fires. Fourteen of these projects are State-sponsored, mostly by Pennsylvania, and one project is sponsored by a non-profit corporation. Seven projects are complete at this writing; however, a summary report must await completion of the remaining projects. The U.S. Bureau of Mines is expected to continue efforts in this field.

These demonstration projects have included, or will include:

1. Exclusion of air from a burning culm pile, using polyurethane foam. After an apparently successful extinguishment, the burning resumed. Cost was about $1.00 per cubic yard.
2. A project similar to the one described above, involving tests with several kinds of plastic coatings to exclude air from the pile, giving special attention to bitumastic coating.
3. Removal of culm bank material by drag line, dumping into a lagoon, removal, repiling and compacting by bulldozers. Cost was about $1.24 per cubic yard.
4. Treatment of a culm pile by injection of a slurry of vermiculite, limestone, and sodium bicarbonate into drill holes sunk into the pile. Results are not announced.
5. Injection of sludge resulting from neutralizing acid mine water with limestone into a burning refuse bank. This treatment, it is hoped, will extinguish the fire and seal the bank.
6. Covering a pile with fine waste dust from cement plants. The following part of the work will involve use of fine limestone dust on the top of the pile.
7. A huge water nozzle that breaks up and extinguishes a burning culm bank. The waste was carried to a water pool and removed with a clam shell for distribution and compaction by carry-alls and bulldozers. The cost was about $0.75 per cubic yard.

5.6.2 Incineration

The average sulfur content of municipal refuse has been found to be about 0.1 percent.[60] Tests made on incinerator stack gases showed SO_2 concentrations generally in the 10- to 30-parts-per-million range.[60] Because of these fairly low values, SO_2 emissions from municipal refuse incinerators are not a major problems and are not usually controlled. Incineration of some high-sulfur chemical wastes is a special problem that should be considered for control along with other elements of the process involved.

5.6.3 Sewage Treatment

Many sewage treatment operations cause odors; however, there are only two sources of SO_2 emissions, sludge-digester-gas combustion and sludge incineration.

Sewage-sludge-digester gas, containing H_2S, is corrosive, which limits its use in internal combustion engines. Hydrogen sulfide concentration at most treatment plants is not above 1 grain per cubic foot of gas,[61] but concentrations have been reported as high as 6 grains per cubic foot[62] where high-sulfate water has entered the sewers. Combustion of H_2S produces SO_2 emissions. Control technology concentrates on removing the H_2S in order to eliminate corrosion. Scrubbing with water or sewage effluent, augmented by adding chlorine to the sewage gas, can reduce H_2S concentrations from over 2 grains per cubic foot to 0.5 grain or less per cubic foot of gas.[61] Treatment of the resulting solution would usually be required before disposal. Another method is the absorption of H_2S on "iron sponge," a mixture of ferric oxide and hardwood shavings.[61,62] The iron sponge is regenerated by exposure to air, releasing the sulfur as SO_2. This has generally been emitted to the atmosphere, but it could be absorbed by alkali solutions.

Sewage sludge is disposed of by various procedures, including lagooning, land filling, using as a fertilizer or a fertilizer base, dumping into the sea, and burning. Since dry digested sludge contains 1 percent sulfur, incineration may produce SO_2 emissions.[63]

A wet oxidation method for sewage sludge, used on a large scale at Chicago, develops SO_2 control as in incidental benefit. In this process, a 3-percent aqueous suspension of ground sludge from the primary settlers is pumped into a heated system where the pressure is about 1800 pounds per square inch and the temperature is about 525°F.[64] Air is injected into the aqueous sludge and "wet combustion" or oxidation occurs. Organics are oxidized to CO_2 and water, or to low-molecular-weight acids such as acetic acid. The sulfur compounds are oxidized to sulfates. Solid residue is about 90 percent inorganic and settles easily from the liquid portion. This liquid portion, which may be only about 1 percent of the total sewage flow, is recombined with the main aqueous flow, and sent to secondary treatment. The heat of oxidation of the sludge is sufficient to make the process thermally self-supporting.

5.7 MISCELLANEOUS SOURCES

5.7.1 Introduction

There are several manufacturing operations, very limited in geographical distribution and scale of production, which are actual or potential sources of SO_2 emissions. There is little published information from which to estimate quantitative emissions for these industries. In most cases, the emissions are relatively minor; however, they may constitute local nuisances.

Sulfur oxide emissions discussed for the following miscellaneous sources are in addition to emissions from fuel combustion.

5.7.2 Glass Manufacture[65]

The glass industry, though large and important, operates in relatively few places.

Sulfur dioxide emissions may occur from the use of salt cake (Na_2SO_4) in the glass tank charge. This material and powdered coal are among the substances charged. The following reaction takes places:

$$\begin{array}{l} Na_2SO_4 + nSiO_2 + C \longrightarrow \\ Na_2O\ nSiO_2 + SO_2 + CO \end{array}$$

No control of gaseous emissions is practiced.

5.7.3 Corn Starch Production

In a typical wet-milling process, corn kernels are steeped in water containing 0.2 percent SO_2 at a temperature of 120°F for 48 hours. This steeping prepares the kernels for separation into starch, gluten, and fibers. Sulfur dioxide is the most effective and most widely used reagent for this purpose. No control of emissions is usually practiced.

5.7.4 Sugar Manufacture

Lime is added to syrup during the sugar manufacturing process to precipitate certain undesirable impurities. Calcium ions in the remaining solution are precipitated by bubbling SO_2 through the syrup to form calcium sulfite. Minor emissions of SO_2 can occur, depending on factors of design and plant operation.

5.7.5 Sulfur Fusion Processes

Processing of batches of sulfur by fusion can emit sulfur oxides at low levels whenever the fusion vessel or kiln is opened. An example is the manufacture of ultramarine, which is made by fusing kaolin, charcoal, sodium carbonate, sulfur, quartz, sodium sulfate, and resin. The melt is removed from the kiln, cooled, ground, and washed. The insoluble compounds are then heated with more sulfur to 950°F until the blue color develops.

5.7.6 Liquid Sulfur Dioxide

The national output of liquid SO_2 in 1964 was 64,237 tons.[66] The gas is produced by burning sulfur or by roasting metal sulfides. The cooled gases, containing up to 18 percent SO_2, are sent to a water absorber.[65] The SO_2 is stripped from the water, cooled, dried, compressed, and liquefied. About 0.02 percent of the total SO_2 is lost into the atmosphere.

5.7.7 Silicon Carbide

Silicon carbide, an important abrasive, is made in an electric furnace at temperatures of 2200°C using sand and coke as raw materials.[65] The furnace has no top, and the walls are temporary so that they can be torn away from the charge after completion of heating. Any gases generated go directly to the atmosphere. The unreacted materials are later separated from the product and recycled as fresh furnace charge.

Any SO_2 evolved in this process will be from the oxidation of sulfur contained in the coke. About 1.4 tons of coke is charged per ton of carbide produced.

5.7.8 Titanium Dioxide

In the manufacture of titanium dioxide, sulfuric acid is added in batches to titanium ore in a digester, yielding primarily titanium sulfate and ferrous sulfate. The digester products are washed and separated, and the ferrous sulfate goes to waste. The titanium compounds enter a calciner where they are heated and converted to titanium dioxide. Sulfur trioxide and sulfuric acid mist are emitted from the calciner. On the basis of field test date, it is estimated that 40 pounds of SO_2 are emitted per ton of titanium oxide calcined.[67] Caustic scrubbers could be used to decrease these emissions by more than 50 percent.

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6. DISPERSION FROM STACKS

6.1 INTRODUCTION

This brief discussion of dispersion from stacks is followed by a bibliography of selected references that provide more complete information.

In general, stacks are used to provide for a reduction of ground-level concentration by giving natural atmospheric turbulence an opportunity to dilute the pollutant before it reaches ground-level receptors. Along with control of emissions, it may be useful to use the natural dilution provided by stacks to obtain desired air quality.

Assuming the same emission rate, ground-level concentration is less with a tall stack than with a short one. Although a stack of any height usually reduces the ground-level concentration, it does not provide a reduction in the amount of material released into the atmosphere nor does it preclude significant concentrations at ground-level under all meteorological conditions. An individual stack may be theoretically high enough to reduce ground-level concentrations to a satisfactory level (if it were the only source); however, it may add its emissions to those from other sources, resulting in undesirable concentration levels. Because the contaminant emission is not reduced, all of it must eventually be removed through natural processes such as washout. The effectiveness of stacks may in some instances be limited by unfavorable terrain.

Current trends are toward larger power plants and higher stacks. These higher stacks are designed to restrict ground-level concentrations to about the same levels as those produced by smaller installations. The possibility of overloading the atmosphere by the sheer size of the installation presents an unanswered question as to the adequacy of even very tall stacks.

6.2 PLUME RISE

In simplifying mathematical treatments of atmospheric dispersion, it is realistic to assume that dispersion begins above the actual stack top at an elevation called the "effective stack height." A number of theoretical and empirical equations have been developed to estimate the magnitude of the plume rise. Since there is no one means of computation that has been generally accepted for all circumstances, professional judgment and experience are required to make the proper choice in a given situation.

When a stack plume is emitted in a disturbed air flow, caused by wind blowing over structures or irregular terrain, standard plume rise and diffusion equations may not apply. Wind tunnel studies with models of stacks, buildings, and other objects are, therefore, used to estimate aerodynamic effects.

6.3 DIFFUSION PROCESSES

For a given set of emission and meterological conditions the expected maximum ground-level concentrations can be estimated as a function of the effective stack height. The important meteorological variables are atmospheric stability and wind direction and speed.

An unstable atmospheric condition occurs when the temperature in the air decreases rapidly with height, as would be expected to happen near the ground during a cloudless day. Conversely, a stable condition exists within a temperature inversion layer, where temperature increases with height. Inversion layers at the ground are most likely to form in rural areas during a night when the sky is clear and winds are light. Within such a layer there is virtually no vertical stack plume diffusion. The effluent trail may be narrow, widening gradually on a straight line from the stack, or it may resemble a meandering river. Plumes from large modern power plants with high stacks generally rise above surface inversion layers into a region of less stability.

Whenever the plume is trapped within the inversion layer, and depending on the duration of the stable period and the wind speed at the effective stack height, the effluent may travel aloft for many miles with relatively slow dilution. However, during the following morning, after the ground has been heated by the sun, air near the ground will be warmed and become turbulent so that parts of the plume are often carried to the ground. This condition, which occurs during the breakup of an inversion layer, is called "fumigation."

Inversion-breakup fumigations are of particular interest with respect to the tall stacks of modern power plants, the plumes of which may reach 1,000 to 2,000 feet. It is generally recognized that fumigation does occur, but its magnitude, extent, and frequency are currently under investigation, and plants generating over 1000 megawatts and utilizing tall stacks are individual cases which require special study.

"The experience of the TVA with their many steam-generating plants illustrates some of these situations. As plants of increasingly larger capacity have been built, with correspondingly taller stacks, the maximum fumigations have shifted from the high-wind type, with which many people are familiar, to the light-wind type. Although tall stacks can be built to minimize the high-wind and inversion-breakup fumigations, the total pollution discharge of the larger plants becomes a problem when the limited capacity of the mixing layer prevents adequate dilution. Thus, the other element that determines concentrations, the pollutant source strength, may require control if such large plants are to be built in parts of the country where this type of fumigation occurs with any appreciable frequency."*

6.4 USE OF MATHEMATICAL-METEOROLOGICAL MODELS

It is necessary to use electronic computers for the large number of dispersion calculations required for estimating air pollution concentrations for an area the size of a city or an air quality control region. In cases where the impact of many sources on numerous receptors is being assessed, even though the interest is primarily in a single source, the analysis is handled best through the implementation of a validated mathematical-meteorological model. By means of such a model, it is relatively easy to consider a change in source conditions (that is, to assume a different sulfur content in fuel, a new stack height, or a different location), and obtain an estimate of the effect. However, the actual value of the result depends upon whether the model has been verified by field observations of concentrations under conditions similar to those assumed in the model.

6.5 METEOROLOGICAL ASPECTS OF SITE SELECTION

A meteorological analysis should be part of the preparation for site selection for an emission source, or for an increase in emission at an established site. The thoroughness of such analyses will vary widely depending on the emission rate of the source and on the nature and number of potential receptors.

6.6 FACTORS FOR SITE EVALUATION

The following list of factors is usually considered when locating a large potential source of air pollution that will use the stack as a means of dispersion.

1. Source Description
   a. Elevation of stack base.
   b. Stack height (physical and effective).
   c. Inside diameter of stack at top.
   d. Stack gas velocity (at top of stack) normally and during slack periods of significant duration.
   e. Stack gas temperature (at top of stack).
   f. Peak, average, seasonal, and diurnal emission rates of SO_2 (grams per second).

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*PHS Publication No. 999-AP-16, Potential dispersion of plumes from large power plants.

2. Climatological Factors Affecting Plume Rise
    a. Air temperature.
    b. Air pressure (for effective stack height computations).
    c. Wind speeds at effective stack height for stability conditions of interest.
    d. Stability conditions in the environment through which the plume is rising. In some cases the frequency of occurrence of each stability type maybe required.
3. Aerodynamic Considerations
    a. Building shapes, dimensions, etc at source.
    b. Nearby large buildings and significant terrain features affecting airflow.
    c. Results of wind tunnel studies, if any.
4. Geography
    a. Description of important terrain features affecting diffusion (using maps, cross sections, etc.)
    b. Locations of populations, present and future, with respect to the source, considering particularly sensitive receptor locations such as hospitals and schools.
    c. Locations of sensitive vegetation or animals, if any.
    d. Adjacent industries that could significantly affect, or be affected by, the source or mutually add to the problems of the area.
5. Other Climatological Factors Affecting Dispersion
    a. Wind direction frequencies at effective stack heights, with consideration of significant seasonal and diurnal variations.
    b. Frequency and duration of light winds and calms.
    c. Local wind circulations (valley winds, sea breezes, etc.)
    d. Stability conditions (frequency of occurrences of stability categories). Consideration should be given to time of day, seasons, and wind direction.
    e. Occurrence of special weather phenomena such as fog.
    f. Precipitation frequency and intensity.
    g. Diurnal and seasonal variation in mixing layer depth, especially in relation to effective stack height.
6. Potential for Increased Emissions
    a. Possible future expansion of existing site.
    b. Possible future construction of other sites.
    c. Effect of expansion and new construction on total emissions.

6.7 OTHER CONSIDERATIONS FOR SITE OR STACK EVALUATION

In some situations where representative meteorological observations are lacking or questionable, a field-observation program may be conducted to obtain on-site data, or to test the representativeness of observations from the nearest weather station.

Effective stack height becomes lower as the wind speed increases, but increased wind speed causes more dilution. Consequently, for a given stability condition there is a critical wind speed for each emission condition at which maximum ground-level concentrations occur. The determination of a critical wind speed simplifies stack design and estimation of a maximum permissible rate of emission, in simple situations where only the maximum concentrations under certain stability conditions are desired.

However, this procedure, if applied alone, neglects the additive effect of the source on the existing background or other emitters in the area. When it is applied, allowance should be made for existing air quality and the possibility of fumigation.

Meteorological assistance with respect to industrial site selection problems may be obtained from professional meteorologists who advertise their services in the Professional Directory section of the Bulletin of the American Meteorological Society. The Executive Director of the Society, (45 Beacon Street, Boston, Mass. 02108) can provide a current list of certified consulting meteorologists.

6.8 STATUS OF POWER PLANT PLUME DISPERSION AND METEOROLOGICAL STUDIES

In order to clarify questions on the dispersion of SO_2 from stacks and the resulting ground-level concentrations and effects, the National Air Pollution Control Administration (NAPCA) is supporting five investigations, in addition to conducting related research through its Meteorology Program.

1. The TVA has been conducting studies of plume rise, inversion breakup, limited mixing layers, and primary and secondary emissions. About 1700 plume rise observations have been taken at six steam plants with stacks ranging from 170 to 800 feet. A tentative conclusion is that with large units and high stacks, maximum ground-level concentration occurs during fumigation associated with a limited mixing layer.
2. NAPCA investigators, in cooperation with the Pennsylvania Electric Company and the Division of Air Pollution Control of the Pennsylvania State Department of Health, are studying stack plume behavior, SO_2 concentrations in the air and on the ground, and effects on flora in the vicinity of three coal-burning electric power generating stations. The first phase of the study is being conducted at the Keystone Power Station, near Indiana, Pennsylvania; subsequent studies will involve the Homer City Station, Homer City, Pennsylvania, and the Conemaugh Power Station, northwest of Johnstown, Pennsylvania. The Keystone Station has twin 800-foot stacks and the Conemaugh Station will have 1000-foot stacks. Observations are being made by means of portable stations, instrumented helicopters, and a laser beam.
3. The GCA Corporation, in a joint study involving Bituminous Coal Research Incorporated, the Edison Electric Institute, and American Petroleum Institute, is investigating the reactions of sulfur compounds in power plant plumes. Quantitative information on reaction rates and products formed will allow the incorporation of SO_2 decay rates into mathematical atmospheric diffusion models. Hopefully it will allow the incorporation of the formation of sulfuric acid mist and inorganic sulfate production into these models.
4. The Argonne National Laboratory, U.S. Atomic Energy Commission, is developing a computer program that will predict the dispersion of SO_2 in the Chicago area. This study considers the requirements of a pollution warning system, measures to be taken to minimize the severity of pollution incidents, and long-ranged city planning.
5. The Brookhaven National Laboratory seeks to determine the feasibility of using the S^{32}/S^{34} ratio of fossil fuels to identify individual sources in urban areas, and determine the decay process of SO_2 to the final end product.

6.9 STACK COSTS

The cost of a stack depends on many factors including size, material and labor costs, and the necessary foundations. Because these costs vary widely, depending on the specific local conditions, only approximate costs can be presented.

Figure 6-1 shows the estimated cost ranges

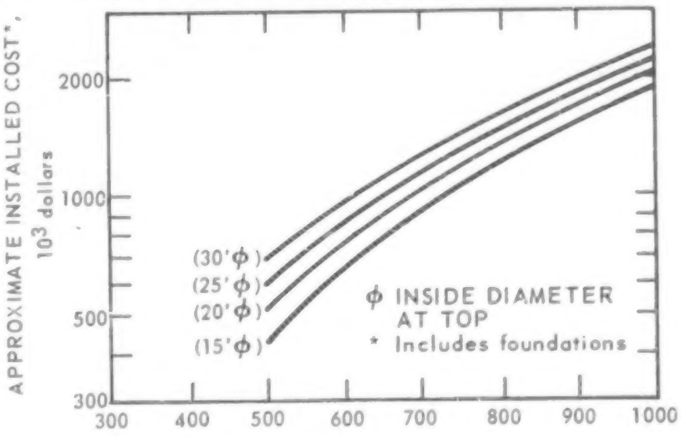

Figure 6-1. Approximate installed costs of stacks.

for stacks of various sizes. These data include only costs directly associated with the stack and not the costs of fans, ducts, or dust collectors.

Operating costs of stacks of various sizes must also be considered. High exit velocities will allow a smaller stack diameter, but also result in higher fan power requirements. Tall stacks today are usually constructed of concrete with low-alloy corrosion-resistant steel liners. This type of stack has proved reliable to date, but long-range maintenance costs are not available, due to the relative newness of these stacks.

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7. EVALUATION OF SULFUR OXIDE EMISSIONS

7.1 COMPILATION OF SULFUR OXIDE EMISSION FACTORS

To determine emission rates, a stack gas analysis of all sources of interest would be necessary. This is, of course, impossible when an air pollution survey covers a large area that might contain many thousands of individual sources. It is often necessary, therefore, to estimate emissions from sources for which accurate stack gas analyses are unavailable. In some cases, the proper use of a good emission factor will yield better results than those based on a single series of stack gas tests. Emission factors are based on past stack gas sampling data, material balances, and engineering estimates for sources that are similar to those in question.

Tables 7-1 through 7-3 are compilations of available emission factors for sulfur compounds from various types of sources. Most of the sulfur emitted is in the form of SO_2, but smaller quantities of SO_3, sulfuric acid mist (usually reported as particulate matter), hydrogen sulfide, and various other forms of sulfur are also emitted. The emission factors listed are for uncontrolled sources and are reported as SO_2 unless otherwise noted. For a specific source where control equipment is used the listed uncontrolled emission rates must be multiplied by 1.0 minus the fractional efficiency of the control equipment. Unless otherwise stated, these factors are based on reference number 1.

Table 7-1. EMISSION FACTORS FOR SULFUR COMPOUNDS FROM FUEL COMBUSTION

Source	Emission factor	
Coal	$38S^{a}\ \frac{\text{lb of } SO_2}{\text{ton}}$	(assumes 5 percent of sulfur remains in ash)
Natural gas	$0.4\ \frac{\text{lb of } SO_2}{10^6\ \text{CF}}$	(assumes sulfur content of $0.14\ \frac{\text{grain}}{100\ \text{CF}}$ of gas)
Process gas	$2.86C^{b}\ \frac{\text{lb of } SO_2}{10^6\ \text{CF}}$	
Fuel oil	$158.8S^{a}\ \frac{\text{lb of } SO_2}{1000\ \text{gal}}$	(includes SO_3; based on fuel density of 8.1 lb/gal)
Wood	Negligible	
Gasoline powered engine	$9\ \frac{\text{lb of } SO_2}{10^3\ \text{gal}}$	(assumed sulfur content of 0.07 percent)
Diesel powered engine	$40\ \frac{\text{lb of } SO_2}{10^3\ \text{gal}}$	(assumed sulfur content of 0.3 percent)
Aircraft	Negligible	

[a] S = percent sulfur by weight.
[b] C = grains of sulfur/100 cubic feet of gas.

Table 7-2. EMISSION FACTORS FOR SULFUR COMPOUNDS FROM SOLID WASTE DISPOSAL

Source	Emission factor, lb of SO_2 per ton of refuse charged
Open-burning dumps and municipal incinerators	1.2–2.0
On-site commercial and industrial multiple-chamber incinerators	1
On-site commercial and industrial single-chamber incinerators	2
On-site residential single-chamber incinerators	0.4
On-site residential flue-fed incinerators	0.2

7.2 SOURCE TESTING FOR SULFUR OXIDES

Emission factors or material balance calculations for sulfur oxides are methods for estimating emissions. However, when it is necessary to quantify the amount of sulfur oxides emitted from a particular source, it is often necessary to perform stack gas sampling.

Many source tests are conducted to determine whether a particular source is complying with emission regulations. Testing for compliance is especially applicable where the theoretical source emission (calculated with

Table 7-3. EMISSION FACTORS FOR SULFUR COMPOUNDS FROM INDUSTRIAL PROCESSES[3,4,5]

Petroleum refineries	See reference 2		
Catalyst regenerators:			
Fluid	0.525 lb/bbl[a]		
Thermofor	0.06 lb/bbl[a]		
Sulfuric acid manufacture	Range: 20–70	lb of SO_2 / ton of 100% acid produced	
Copper smelting—primary	1250	lb of SO_2 / ton of concentrated ore	
Lead smelting—primary	660	lb of SO_2 / ton of concentrated ore	
Lead smelting—secondary cupola	64	lb of sulfur compounds / ton of metal charged	
Lead smelting—secondary reverbatory and sweat furnaces	149	lb of sulfur compounds / ton of metal charged	
Zinc smelting—primary	530	lb of SO_2 / ton of concentrated ore	
Iron and steel mill sinter machine	0.3	lb of SO_2 / ton of ore	(assumes ore content of 0.01 percent with 71 percent of sulfur going up stack)
Ammonia purification at coking plant	8.7	lb of SO_2 / ton of NH_3 solution	
Pulp and paper mills:			
Kraft type—recovery furnace	2.4–13.4	lb of SO_2 / ton of air dried pulp	
Sulfite type—recovery furnace	40	lb of SO_2 / ton of air dried pulp	(assumes 90-percent recovery of SO_2)
Calcium carbide manufacturing—main stack with impingement scrubber	2.54	lb of SO_2 / ton of product	(includes SO_3)
Coke dryer	0.25	lb of SO_2 / ton of product	(includes SO_3)

[a] Based on data from Los Angeles. Could be considerably different in other areas, depending on sulfur content of the feed stocks.

emission factors or by material balance) approximates the code limitation. Source tests are also performed to determine the true efficiency of emission control devices, especially where the theoretical collection efficiency would result in a narrow margin of compliance. Where alterations in a process design may be needed to correct pollution, source test results are often used as a basis for suggesting changes and to identify those changes which will be most effective. Another use of source test data would be in the determination of how great a theoretical reduction in pollution could be expected from the initiation of a proposed code.

The following methods are most commonly used in source testing:

1. Shell Development Company Method.[6, 7]
2. Los Angeles County Air Pollution Control District Method.[8]
3. Total sulfur oxides, API Method 774-54.[9]
4. Retch Test for sulfur dioxide.[10]
5. Bureau of Mines Method No. 4618 for sulfur dioxide and sulfur trioxide.[11]
6. Determination of sulfuric acid mist, sulfur dioxide, and sulfur trioxide.[12]

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Appendix—Chemical Coal Processing

1. INTRODUCTION

A brief summary of chemical coal processing was presented in Section 4.4.1. This appendix presents more detailed information on these processes.

2. LIQUEFACTION OF COAL

The Pemco Process of solvent refining of coal yields a low-sulfur, low-ash fuel. At room temperature, the fuel is a shiny black solid which is hard and brittle and can be readily ground into an extremely fine powder. Since this fuel liquifies as approximately 430°F, it can be burned as either a solid or a liquid.

The solvent refining process, while strictly speaking not a coal liquefaction process, is shown in Figure A-1. In this process, finely ground coal and anthracene oil are slurried, hydrogen is added to prevent repolymerization, and the mixture is heated to 840°F. The dissolved coal is filtered to remove the ash residue containing pyritic sulfur mixed with

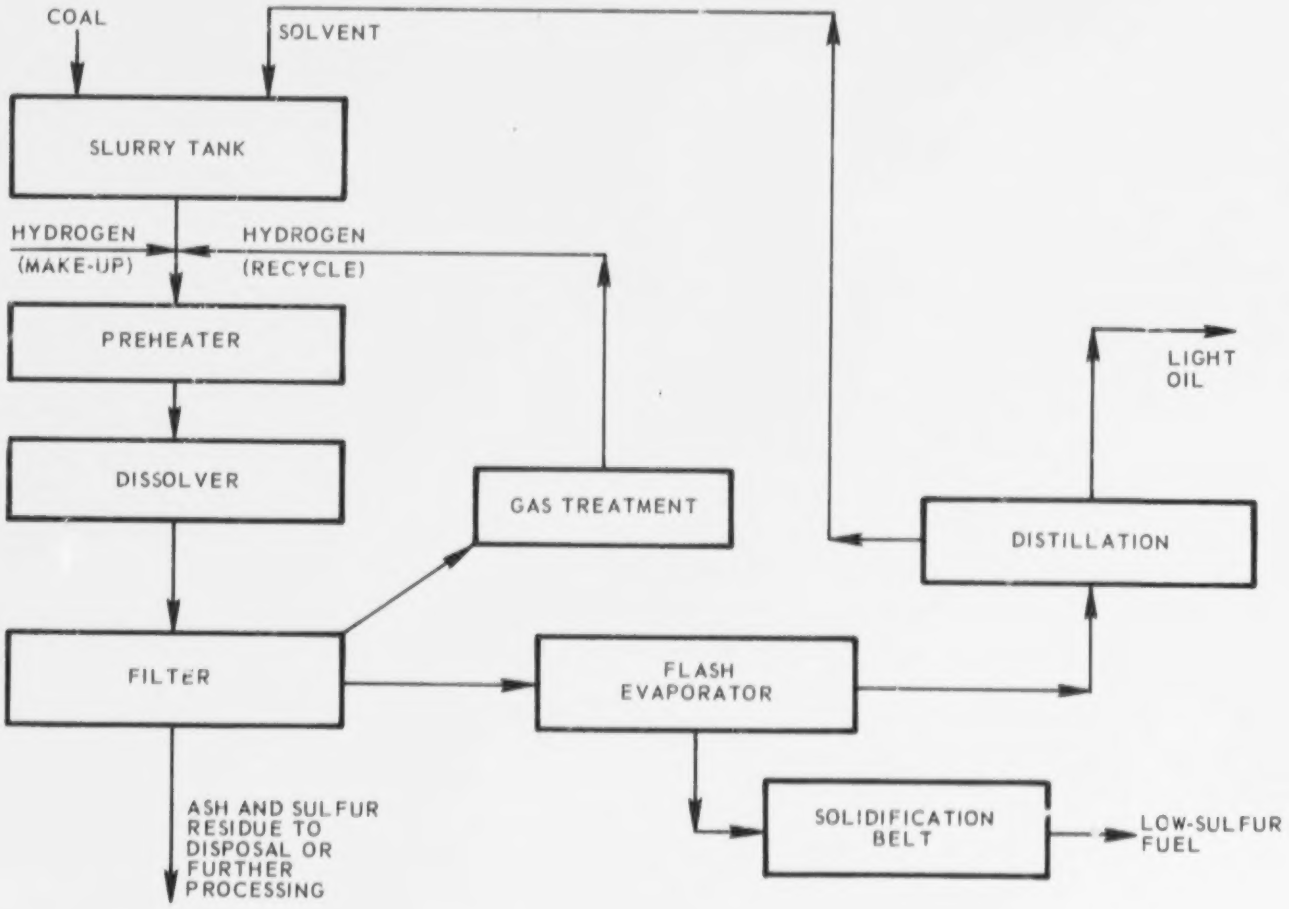
COAL
SOLVENT
SLURRY TANK
HYDROGEN (MAKE-UP)
HYDROGEN (RECYCLE)
PREHEATER
DISSOLVER
GAS TREATMENT
LIGHT OIL
DISTILLATION
FILTER
FLASH EVAPORATOR
SOLIDIFICATION BELT
LOW-SULFUR FUEL
ASH AND SULFUR RESIDUE TO DISPOSAL OR FURTHER PROCESSING

Figure A-1. Solvent refining (simplified flow chart).

other separated minerals. Unused hydrogen is recycled. The filtered coal solution is flash-evaporated to remove the light fraction. This process allows the solvent to be recovered after distillation and yields some light oil. The hot liquid residue from the evaporator is discharged and cooled to yield a unique fuel product.

Final product properties depend on the raw coal. Typical feed and product yields are shown in Table A-1.

Table A-1. SOLVENT REFINED COAL PRODUCT[1]

	Raw coal (Kentucky #11)	Refined product
Ash, percent by weight	6.91	0.11
Sulfur, percent by weight	3.27	0.95
Heat content, Btu/lb	13,978	15,956

Coal containing predominantly pyritic sulfur can be converted by this process to a refined fuel with a low sulfur content because the pyritic sulfur is removed with the ash in the filtration step. Up to 70 percent of the organic sulfur may be removed by hydrogenation to H_2S in the dissolving step. More solvent is generated than is used, so this step is economically attractive and also adds flexibility to the final product by allowing admixture with the solvent.

Considerable market development is required to establish uses for this fuel. Processing costs have been estimated at about 19 cents per million Btu, and total cost at 27 to 32 cents per million Btu.[1]

A 100-pound-per-hour pilot plant has been completed and a large installation is planned for Tacoma, Washington, for 1969.

FMC Corporation's Project COED (char-oil-energy development), the Office of Coal Research's oldest coal liquefaction project, began work in May 1962. This process, which begins with a carbonization step, produces a liquid, some gas, and char as shown in Table A-2.

Table A-2. TYPICAL PRODUCT YIELDS FOR COED PROCESS

(Based on Utah A Seam King Coal)

Product	Weight percent
Char	54.3
Oil	23.6
Gas	15.0
Tar liquor	7.0

In the COED process, diagramed in Figure A-2, crushed coal is heated to progressively higher temperatures in a series of four fluidized bed reactors. From 1 to 5 percent of the charge is volatilized in the first stage, and 50 percent of the oil yield is derived from the second stage. Burning a portion of the char with oxygen in the last stage supplies process heat. All the volatile products from the coal produced by the last three stages exit from the second stage to the product recovery system. The gas, containing 40 to 50 percent hydrogen, can be processed further to produce methane or hydrogen. Oil processing yields conventional gasoline and fuel oil products.

Technology has progressed through the operation of a 100-pound-per-hour process development unit. Design of a 36-ton-per-day prototype plant is underway, and operation is scheduled for 1970.

Oil yields are relatively high, from 1 to 1.5 barrels per ton of coal. The problem of effective use of the large amount of char has led FMC to develop a process for removal of sulfur from the char so that it might be used as a low-sulfur boiler fuel in power plants.

The essential elements of this desulfurization process are shown in Figure A-3. The key part of the process is the use of calcined dolomite ($CaO + MgO$) as an "acceptor" to absorb sulfur from the liberated H_2S. Char and acceptor are easily separated because of the large particle size of the acceptor. Sulfur is desorbed from the acceptor at 800°F by reaction with steam and CO_2:

$$(CaS + MgO) + H_2O + CO_2 \longrightarrow (CaCO_3 + MgO) + H_2S.$$

Hydrogen sulfide is converted to elemental sulfur in a Claus system, and the acceptor regenerated by calcining at 1600°F.

FMC has estimated that the cost for reduction of sulfur level in char from 3 percent to 0.3 precent is about 10 cents per ton of char, or about 0.4 cents per million Btu.[2] These figures allow substantial credit for

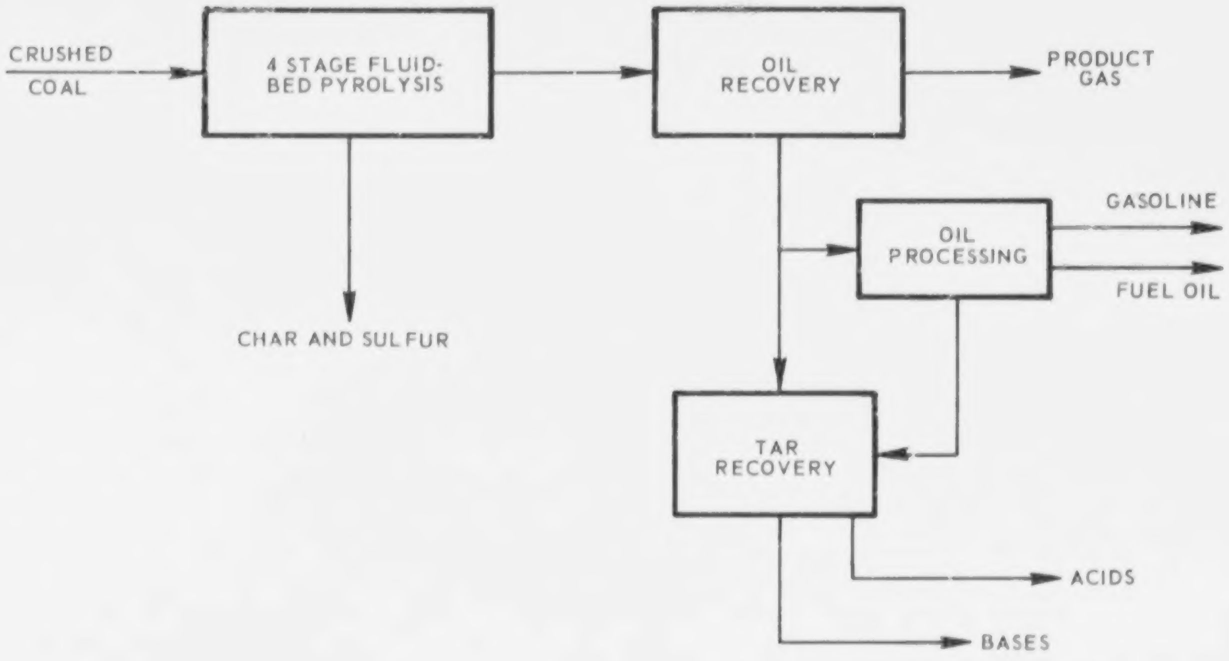
CRUSHED
COAL
4 STAGE FLUID-BED PYROLYSIS
OIL RECOVERY
PRODUCT GAS
GASOLINE
OIL PROCESSING
FUEL OIL
CHAR AND SULFUR
TAR RECOVERY
ACIDS
BASES

Figure A-2. COED process (simplified flow chart).

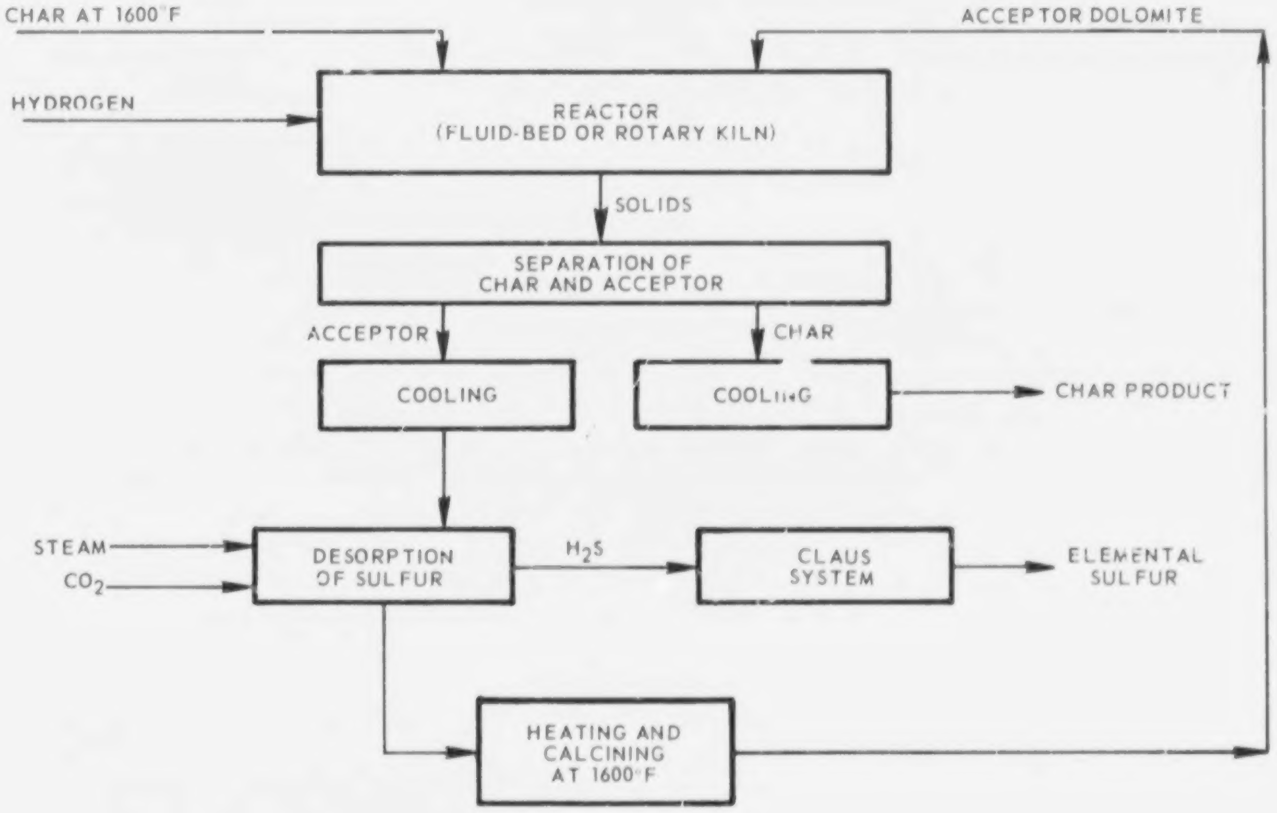
CHAR AT 1600°F
ACCEPTOR DOLOMITE
HYDROGEN
REACTOR
(FLUID-BED OR ROTARY KILN)
SOLIDS
SEPARATION OF
CHAR AND ACCEPTOR
ACCEPTOR
CHAR
COOLING
COOLING
CHAR PRODUCT
STEAM
CO_2
DESORPTION
OF SULFUR
H_2S
CLAUS
SYSTEM
ELEMENTAL
SULFUR
HEATING AND
CALCINING
AT 1600°F

Figure A-3. Desulfurization of coal char (FMC process).

sulfur recovery (60 cents for each ton of char processed).

The major disadvantage of the process is the present lack of use for the char product. Considerable market development will be required to establish its usefulness.

The H-Coal process, developed by Hydrocarbon Research, Inc., uses hydrogenation to recover a light crude oil which can be conventionally refined to gasoline. Coal conversion rate is higher than for other methods, as shown in Table A-3 for Illinois #6 coal on a moisture- and ash-free basis.

Table A-3. PRODUCT YIELD FOR H-COAL PROCESS

(Illinois #6 coal)

Product	Percent of original coal by weight [a]
Light gas	10.2
Liquid product	71.0
Char	10.7
H_2S, NH_3, H_2O	8.1

[a] Moisture and ash free basis.

This shows that about 90 precent by weight of the moisture- and ash-free coal is converted in the reactor.

In the H-Coal process, diagrammed in Figure A-4, coal is dried, pulverized, slurried with coal-derived oil, and charged continuously with hydrogen to a reactor containing a bed of ebullating catalyst (fluidized bed where the liquid is the fluidizing medium). The coal is hydrogenated and converted to gaseous and liquid products: refinery gases, naptha, middle distillate, and heavy gas oil. The unconverted coal residue and the heavy liquid product are sent to the carbonization section. Recovered heavy gas oil is catalytically hydrocracked to middle distillate, naptha, and refinery gas. The naptha is further treated and reformed to gasoline.

Ammonia, and a portion of the hydrogen sulfide produced in the coal and heavy-gas-oil hydrogenation steps, are recovered as an aqueous solution of ammonium sulfides. This solution, together with the H_2S recovered from the refinery gases, is treated to convert the ammonium sulfides into ammonia and H_2S. The H_2S may be further processed to sulfuric acid. The ammonia is converted with a portion of the sulfuric acid to ammonium sulfate.

Although this process does produce low-sulfur products, the economics of the process are very sensitive to the price of light fuel oil and gasoline. Recent estimates place the cost of the oil between 12.1 and 14.3 cents per gallon, depending on the size of the plant.[6]

Bench-scale work with a reactor processing 15 to 25 pounds per day of coal has been completed. A 3-ton-of-coal-per-day pilot plant has been in operation since February 1966, and the next step will be a demonstration unit, using 250 to 500 tons of coal per day, located in a coal producing area.

The most extensive effort of the Office of Coal Research (OCR) to liquefy coal is the Consol (CSF) process, developed by Consolidation Coal Company to enable gasoline from coal to compete with its petroleum counterpart in coal producing areas. In this process, diagrammed in Figure A-5, coal is dissolved in a process-generated liquid, and ash and other non-reactive parts are filtered out. Solids go to a low-temperature carbonization step, which recovers solvent and produces char. Liquids are first distilled to recover solvent, light distillate, and a heavier fraction. The heavier fraction is hydrogenated and distilled to form the major crude-oil portion. The crude oil is sent to the gasoline-making step.

OCR feels that for a large commercial plant (30,000 to 100,000 barrels of gasoline per day) a projected product cost of 11 cents per gallon is realistic. Uses for the char and availability of low-cost hydrogen are major considerations. These considerations make the building of such gasoline plant next to a Consol coal-gasification plant attractive, because this would allow some char use and provide a source of low-cost hydrogen.

The CSF process is the biggest OCR liquefaction process and the most technologically advanced. A pilot plant, in operation since May 1967, at Cresap, West Virginia, is capable of processing 1 ton of coal per hour, resulting in a liquid output of 60 barrels daily. Design of a commercial plant may start in the early 1970's if all goes well at Cresap.

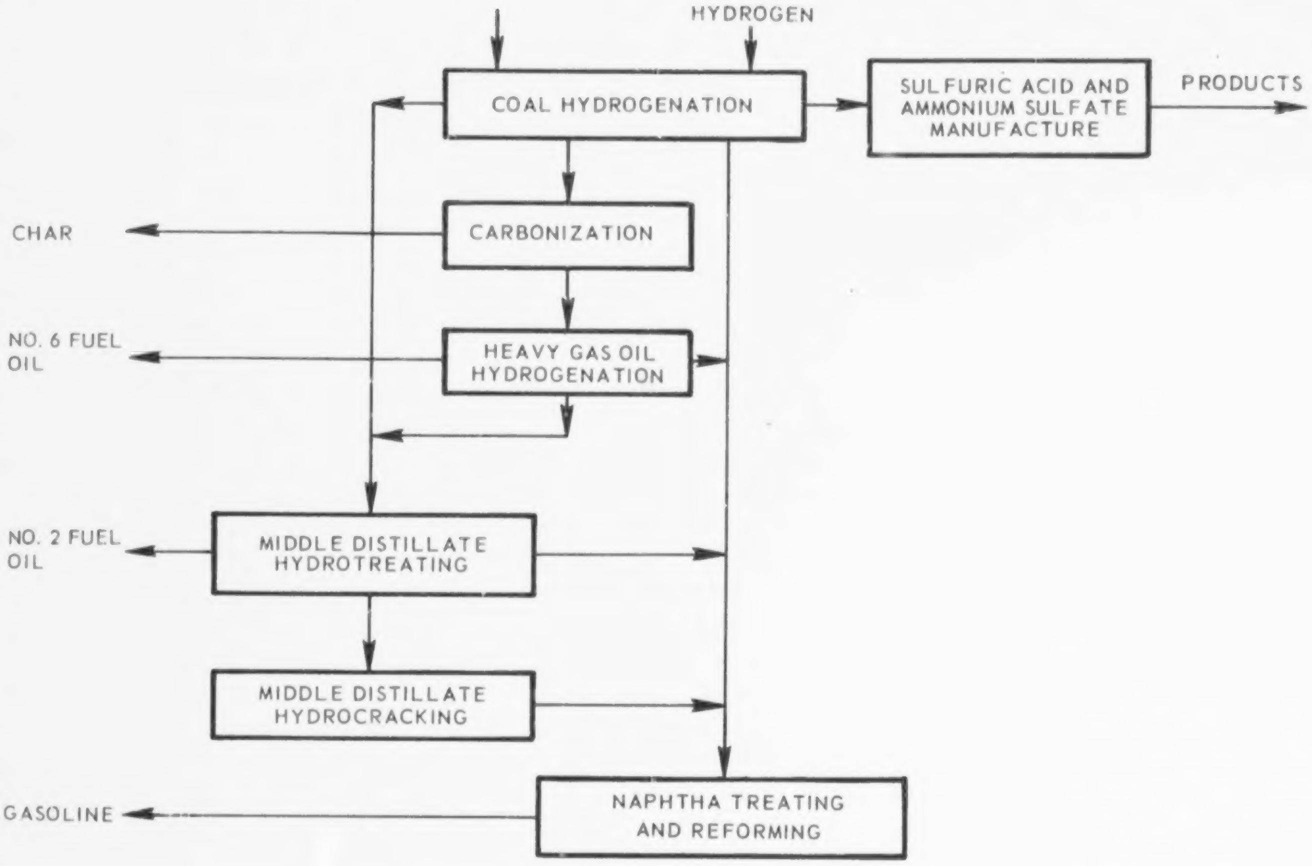
HYDROGEN
COAL HYDROGENATION
SULFURIC ACID AND AMMONIUM SULFATE MANUFACTURE
PRODUCTS
CARBONIZATION
CHAR
NO. 6 FUEL OIL
HEAVY GAS OIL HYDROGENATION
NO. 2 FUEL OIL
MIDDLE DISTILLATE HYDROTREATING
MIDDLE DISTILLATE HYDROCRACKING
GASOLINE
NAPHTHA TREATING AND REFORMING

Figure A-4. H-Coal process (simplified flow chart).

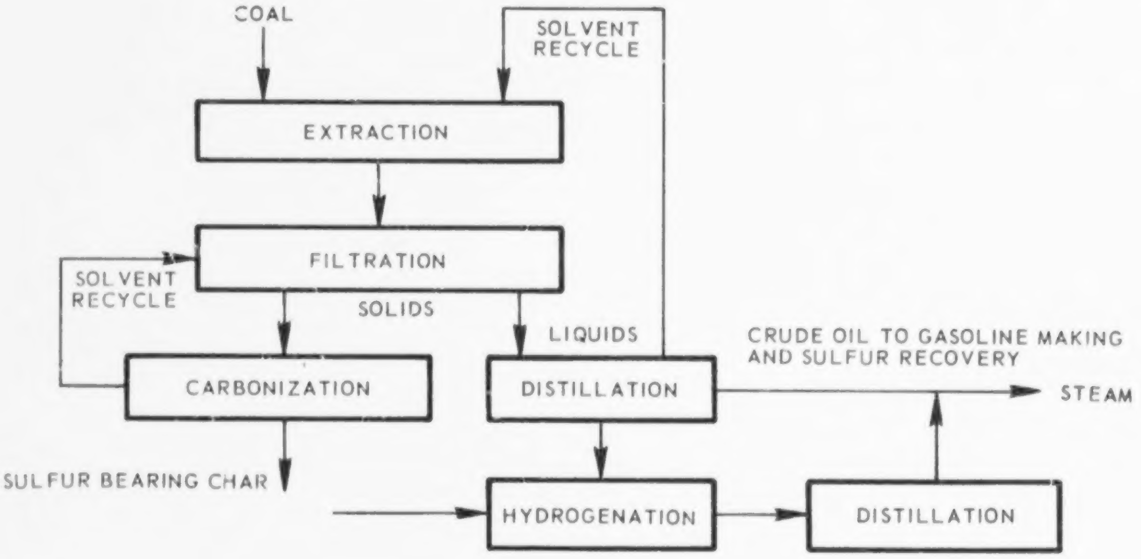
COAL
SOLVENT RECYCLE
EXTRACTION
FILTRATION
SOLVENT RECYCLE
SOLIDS
LIQUIDS
CARBONIZATION
DISTILLATION
CRUDE OIL TO GASOLINE MAKING AND SULFUR RECOVERY
STEAM
SULFUR BEARING CHAR
HYDROGENATION
DISTILLATION

Figure A-5. CSF process (simplified flow chart).

GASIFICATION OF COAL

Hydrogasification, diagrammed in Figure A-6, is essentially a two-stage, high-pressure, direct reaction of treated coal with hydrogen to form methane. The coal is ground in a hammer mill before being partially oxidized. This partial oxidation overcomes the tendency of the coal to agglomerate during hydrogasification. The high pressure (1100 psig) hydrogasification is divided into two distinct reaction zones. The pretreated coal first enters a free-fall, low-temperature (900°F to 1300°F) zone; then, by moving-bed, the unreacted portion of the coal enters the high-temperature (1700°F) zone where further gasification occurs. The lower temperature zone favors formation of methane from the volatile portion of the coal, and the higher temperature zone favors the formation of hydrogen and carbon monoxide.

Gas produced in the low-temperature zone of the hydrogasifier passes through purifying steps for removal of carbon dioxide, hydrogen sulfide, and traces of organic sulfur. The purified gas is then enriched to pipeline quality by methanation using carbon monoxide and hydrogen from the hydrogasifier. After excess water vapor is removed, the resultant gas is ready for distribution to consumers.

The Institute of Gas Technology has carried cut developmental work on hydrogasifi-

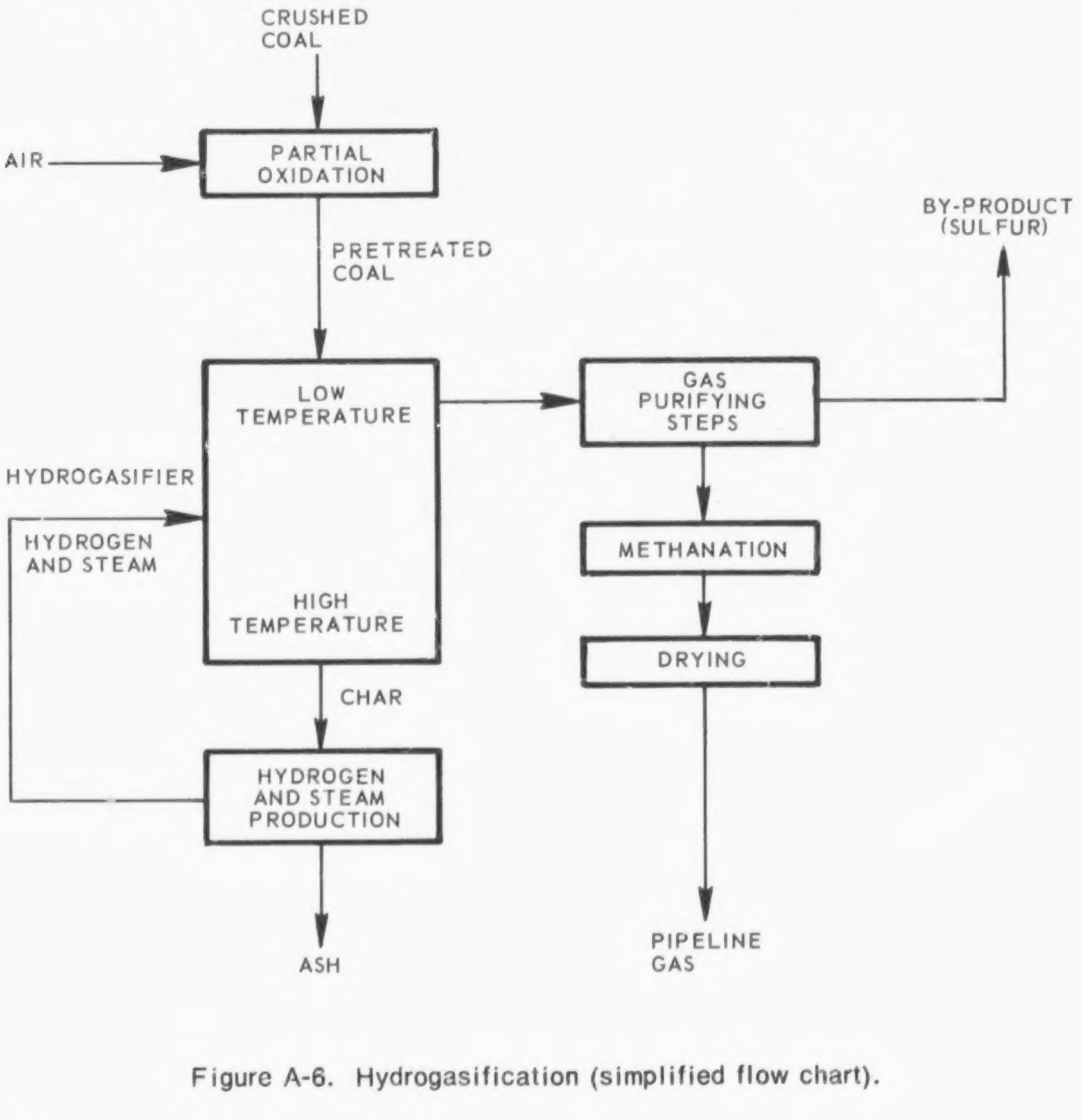
CRUSHED COAL
AIR
PARTIAL OXIDATION
PRETREATED COAL
BY-PRODUCT (SULFUR)
LOW TEMPERATURE
GAS PURIFYING STEPS
HYDROGASIFIER
HYDROGEN AND STEAM
METHANATION
HIGH TEMPERATURE
DRYING
CHAR
HYDROGEN AND STEAM PRODUCTION
ASH
PIPELINE GAS

Figure A-6. Hydrogasification (simplified flow chart).

cation, and has completed a pilot-plant study.[5,6] A prototype plant is tentatively scheduled for completion in 1970, and a commercial plant by 1975. The work is supported by the American Gas Association (AGA) and the U.S. Government Office of Coal Research (OCR).

Hydrogasification is perhaps the most promising method for obtaining pipeline quality gas. Present cost estimates are based on an overall thermal efficiency of about 75 percent. One of the major cost factors is the requirement for hydrogen. Current development by the Bureau of Mines of various methods of using the spent char for hydrogen production could reduce overall costs. Additional pilot-plant experience, and the recovery value of the sulfur from gas purification, should also reduce overall costs in the future. Ultimately, OCR expects the gas to cost between 35 and 50 cents per million Btu.

Consolidation Coal Company (Consol) is advancing its CO_2 acceptor process to the pilot-plant stage.[7,8] The Office of Coal Research has sponsored the work since mid-1964. Consol has subcontracted with the M. W. Kellogg Co. for design of the pilot plant to be built in Rapid City, South Dakota. Operations should begin within 1½ years, with an initial feed of lignite coal of 30 tons per day.

In the CO_2 acceptor process, diagrammed in Figure A-7, lignite coal is crushed, dried, and preheated before entering a devolatilizer operated at about 1400°F and 285 psig. The coal is devolatilized by contact with the gasi-

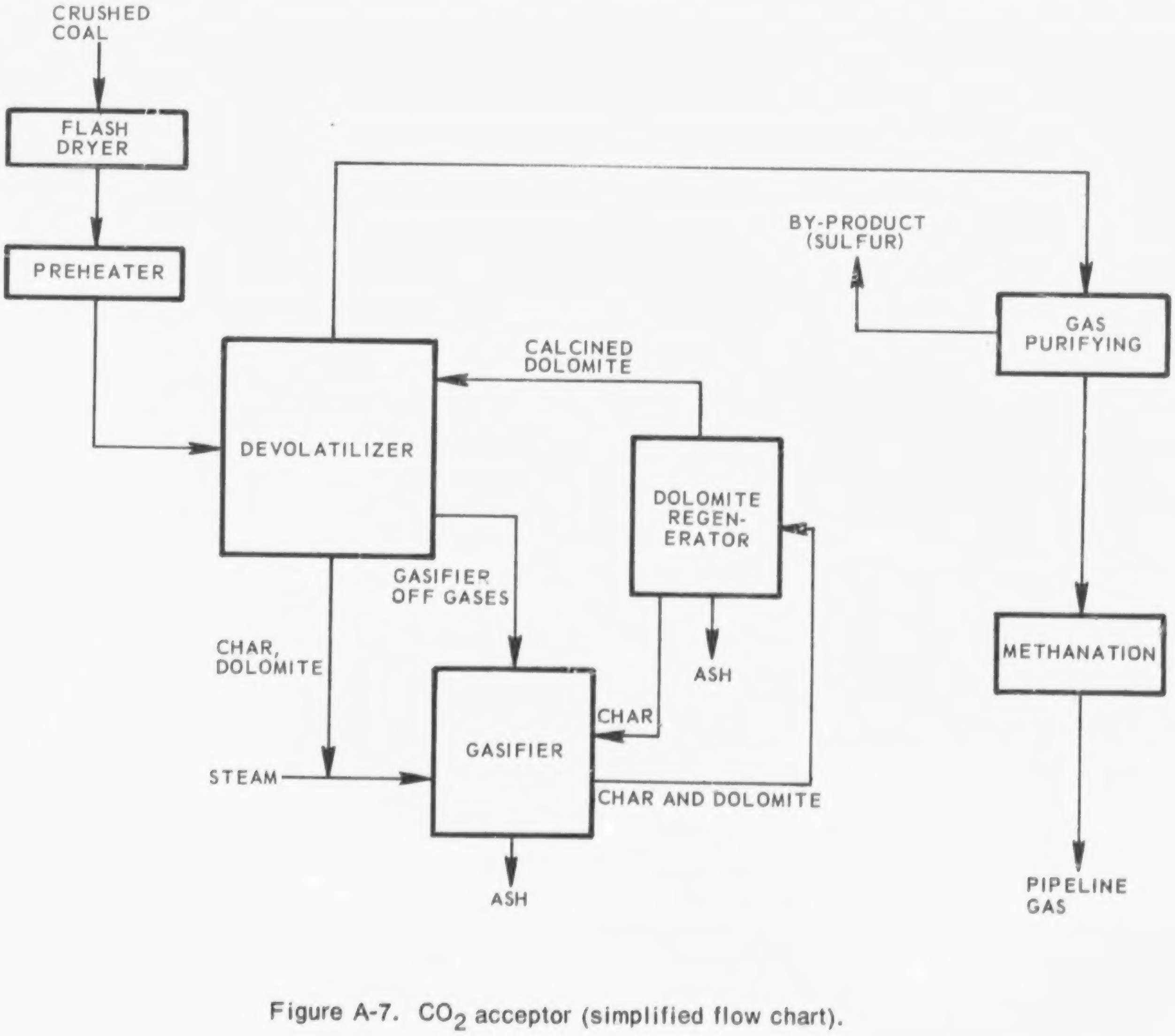
CRUSHED COAL
FLASH DRYER
PREHEATER
DEVOLATILIZER
CALCINED DOLOMITE
DOLOMITE REGEN-ERATOR
BY-PRODUCT (SULFUR)
GAS PURIFYING
GASIFIER OFF GASES
CHAR, DOLOMITE
ASH
METHANATION
CHAR
GASIFIER
STEAM
CHAR AND DOLOMITE
ASH
PIPELINE GAS

Figure A-7. CO_2 acceptor (simplified flow chart).

fier off-gases and is mixed with the calcined-dolomite CO_2 acceptor. Superheated steam carries the devolatilized char and dolomite to the gasifier, where 60 percent of the carbon in the char is gasified at 1600°F. Heat required for this gasification is supplied by the dolomite's acceptance of the CO_2 formed during gasification. The dolomite (now in the carbonate form) is returned to the regenerator for calcining. Heat for regeneration of the dolomite is supplied by combustion of compressed air with the residual char from the gasification stage.

After the gas from the devolatilizer is purified, it requires some methanation to bring it up to pipeline-gas quality. It should be noted that the reaction of the lime with the CO_2 makes gasification possible without the presence of oxygen. The resulting gas stream is further concentrated by removal of the CO_2.

This process produces not only high-Btu gas, but also low-sulfur fuel (char) and low-cost, high-purity hydrogen. With nearby markets for the major products, this process could be commercially feasible in a few years. It is especially attractive when combined with a coal liquefaction plant requiring low-cost, high-purity hydrogen.[9]

The M. W. Kellogg Company has carried the molten salt process into bench-scale experimentation under a contract with the Office of Coal Research.[7] Under a contract awarded in June 1964, Kellogg is making a concurrent engineering-cost evaluation. No funds have been allocated in fiscal year 1968-69 for this process.[9]

Like the CO_2 acceptor process, the molten salt process eliminates the need for oxygen or air in the gasifier unit. Dilution of the raw gas by the non-reactive portion of air is undesirable since this leads to costly purification. In this process, diagrammed in Figure A-8, a molten salt such as sodium carbonate supplies reaction heat and acts as a catalyst for the gasification reaction.

The gasifier, operated at 1000°F and 430 psig at the coal inlet and 1700°F and 400 psig at the gas outlet, is divided into two sections by a vertical partition. The partition is perforated below the surface level of the molten salt so that the salt can circulate but the gas evolved on one side cannot be carried over to the other. The coal and steam enter on one side of the partition, and preheated air enters on the other. The coal residue carried through the partition by the molten salt is oxidized by the air to supply heat for the gasification reaction taking place in the other half of the reaction vessel. The gasification reaction is further enhanced by the catalytic properties of the molten salt, which lowers the required reaction temperature and optimizes methane formation. Because of problems associated with the two-part gasifier, it has been designed as two separate units, one for gasification and one for coal combustion. In either design, the coal combustion gases and gasification gases are separated, but heat transfer is allowed.

The relatively high temperature requires a system of heat recovery, as shown in Figure A-8. Effective removal of coal ash from the molten salt requires more development, as does most of this process. Work to date does not provide a basis for estimation of the extent of gas purification and enriching (further methanation) that will be required.

Although the CO_2 acceptor and molten salt processes eliminate the need for costly high-purity oxygen or hydrogen, the capital investment in either is quite high. Systems for regeneration of the salt or dolomite and for required auxiliary control need much refinement.

Bituminous Coal Research, Inc. (BCR) has been moving toward refinement of the two-stage superpressure coal gasification process.[7] BCR's original contract with OCR, awarded in December 1963, was extended by 30 months in November 1966. The bench-scale work has been completed, and a 100-pounds-of-coal-per-hour process and equipment development plant is under construction.

The process, diagrammed in Figure A–9, is based on a high-pressure two-stage gasifier in which most of the volatile portion of the coal is converted directly to methane and the residual char is reacted with oxygen and steam to supply process heat. This gasification process may require less investment in equipment than either the CO_2 acceptor or molten salt processes and requires less high-purity oxygen than hydrogasification.

A high-volatile bituminous coal is injected into stage 2 of the reactor vessel and there heated rapidly to 1700°F and 1050 psig. Methane formation is rapid, and the non-volatile portion of the coal is returned to stage 1, which is essentially a slagging gasifier. High temperature and pressure optimize formation of methane (about 23 percent in the raw gas). The raw gas is cleaned by passage through cyclones, and the entrained, low volatile char is recycled to stage 1 of the gasifier.

Since this process is in early stages of development, evaluation of its feasibility is difficult. However, because of the temperature involved, a system of heat recovery similar to that used in the molten salt process will probably be necessary. The main problem in the operation of this superpressure process will be to keep the pressures and temperatures in various parts of the gasifier at optimum operating values.

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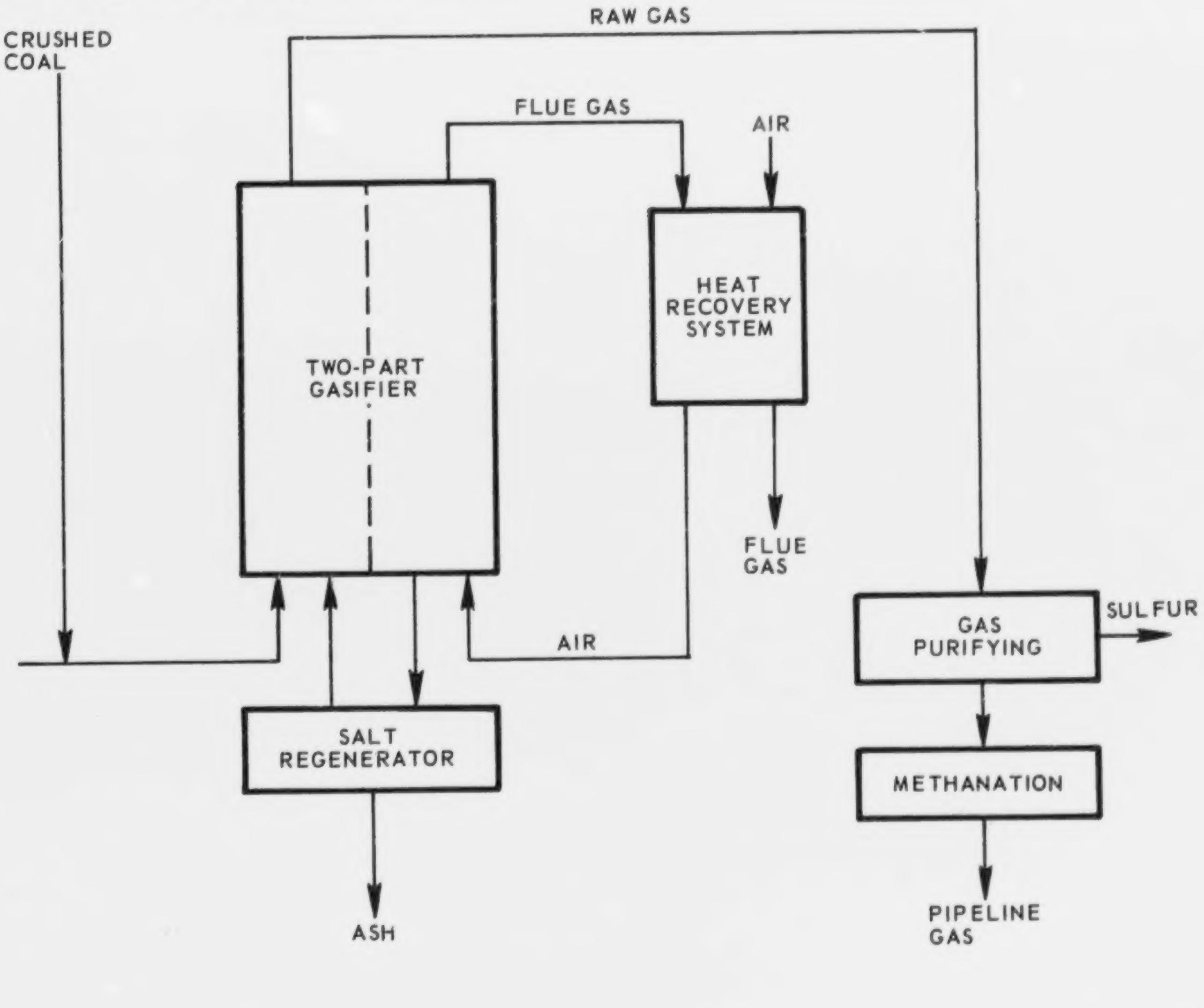
RAW GAS
CRUSHED COAL
FLUE GAS
AIR
HEAT RECOVERY SYSTEM
TWO-PART GASIFIER
FLUE GAS
AIR
GAS PURIFYING
SULFUR
SALT REGENERATOR
METHANATION
ASH
PIPELINE GAS

Figure A-8. Molten salt (simplified flow chart).

4. "OCR Points Liquid Coal to Market." Coal Research, No. 24, Autumn 1966.
5. "Process Design and Cost Estimate for Production of 266 Million scf/day of Pipeline Gas by the Hydrogasification of Bituminous Coal—Hydrogen by the Steam-Iron Process." Office of Coal Research Contract 14-01-0001-381, Washington, D. C.
6. "Compilation of Interim Reports on Projects for the Production of Pipeline Quality Gas from Coal." Office of Coal Research, Washington, D. C.
7. "Pipeline Gas from Lignite Gasification—A Feasibility Study." Office of Coal Research Contract 14-01-0001-415, Washington, D. C.
8. Cochran, N. Private communication, April 1968.
9. "Laboratory-Scale Flow Reactor for Studying Gasification of Coal under Conditions Simulating Stage 2 of the BCR Two-Stage Super-Pressure Gasifier." Preprint (Presented at the American Institute of Chemical Engineers Symposium, Carnegie Institute of Technology, Pittsburgh, Pa., April 7, 1967.)

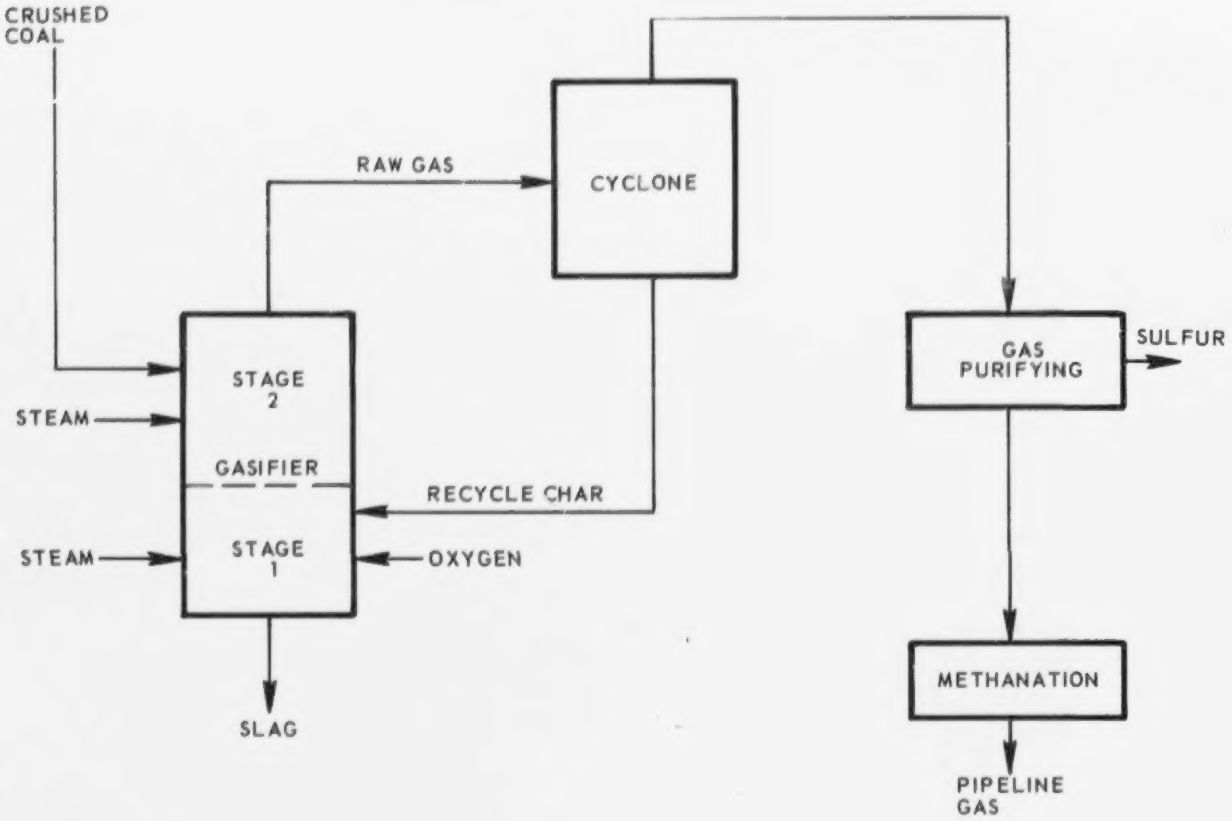
CRUSHED COAL
RAW GAS
CYCLONE
STAGE 2
STEAM
GASIFIER
RECYCLE CHAR
STEAM
STAGE 1
OXYGEN
SLAG
GAS PURIFYING
SULFUR
METHANATION
PIPELINE GAS

Figure A-9. Two-stage, super-pressure desulfurization process (simplified flow chart).

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